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METHODS OF ANALYSING SAMARSKITE

AND THE OTHER COLUMBATES CONTAINING EARTHY OXIDES, BY THE AGENCY OF FLUORHYDRIC ACID; AND OF DISSOLVING COLUMBITE AND TANTALITE BY THE SAME ACID.—ON THE SEPARATION OF THORIA FROM THE OTHER OXIDES.—QUANTITATIVE ESTIMATION OF DIDYMIUM OXIDE IN ITS MIXTURES WITH OTHER EARTHY OXIDES.

BY J. LAWRENCE SMITH, *Louisville, Ky.*

[*Concluded from p.* 51.]

Earths from Samarskite.

As it has been necessary to use letters to indicate the various groups of constitutents of this mineral, they will be stated in a list, for easy reference:

A—The portion of samarskite soluble in fluorhydric acid.

B—The portion of samarskite insoluble in fluorhydric acid.

C—The mixed oxalates of the earths from samarskite.

D—The earthy oxides insoluble or dissolved with difficulty by the sulphate of potassium or sodium.

From the time that samarskite was discovered until I undertook the examination of the mineral as it was found in Mitchel county, N. C., the earths from the ignited oxalates were considered to be the oxides of the cerium group and yttria group, and in my researches made in 1876 and 1877, while I referred to one of these

oxides as cerium oxide, in a footnote[1] I stated that there were grounds for belief that the oxide so called was not cerium oxide, as it was completely soluble in a very dilute solution of nitric acid.

A little later, by repeated precipitation of this oxide (as prepared from samarskite) with sodium sulphate I obtained an oxide, the sulphate of which is absolutely insoluble in a concentrated solution of the sulphate. The oxide of this was completely soluble in very dilute nitric acid. In many respects it resembled cerium oxide. Among them it did not furnish any absorption ray in the spectrum, but its complete solubility in very dilute nitric acid was a marked distinction between it and cerium oxide. For this reason I considered it a new oxide and called it mosandrum. The atomic weight of the oxide was made out to be 109 (O = 16).

M. Marignac, however, as well as Prof. Delafontaine, was inclined to regard the oxide as terbia. The properties of this latter earth were never clearly understood, yet as far as I had been able to make them out I considered it to differ from what I had called mosandrum. Not having any absorption ray, it is not so easy to decide upon as upon most of the earthy oxides.

The study instituted upon the earths coming from samarskite opened a new field of investigation upon the earths of the cerium and yttrium groups, especially among those which gave marked and decided absorption rays. As yet they cannot be separated in a pure state in sufficient quantity for a complete chemical study, at least so far as my information at the present time goes.

Prof. Delafontaine, of Chicago, has done some excellent work on these earths, among which he considers that he has discovered two metals that are new, phillipium[2] and decipium. In regard to the first, the spectroscopic and other characteristics are well defined, so much so that those chemists and physicists who have examined it, as MM. Marignac, Soret and Lecoq de Boisbaudrant, have no doubt upon the subject. As regards decipium,[3] the spectroscopic examination of Soret and Lecoq de Boisbaudrant has not as yet furnished us with any positive decision, as far as my information extends at the present time; M. Delafontaine, however, feels satisfied about it.

In addition to the above, M. Marignac has separated another, working, however, on gadolonite and euxinite, which he calls ytterbium,[4] and L. F. Nilson another, which he calls scandium,[5] and

[1] Amer. Jour. Science, May 1877. [2] Comptes rendus, 1878, **86**, 559. [3] *Ibid.* 632.
[4] *Ibid.* 1879, **87**, 578. [5] *Ibid.* 645.

believes to be associated with the ytterbium of Marignac. It is determined by spectroscopic examination of a somewhat complicated nature. I would here state that most of these new earths have only been made out by a very small quantity, sometimes less than a gram, the spectroscopic work being done by the most skillful observers.

The use of the spectroscope in studying the earths requires great care, and sometimes the presence of a very minute quantity of some foreign substance may lead to wrong conclusions. Thus the presence of traces of uranium caused Sorby to mistake zirconia for a new oxide that he called jargonia, and some similar cause induced Delafontaine[1] to consider that there was a marked difference between the didymium oxides of cerite and samarskite, didymium oxide of cerite being a mixture of different earths. Soret,[2] however, showed that the didymium oxide from samarskite, as furnished him by Marignac, was the same as that from the oxide from cerite. Lecoq de Boisbaudrant came to the same conclusion from the oxide I had furnished him as coming from samarskite. A still more curious fact is that, in some experiments I made in connection with Lecoq de Boisbaudrant, a peculiar treatment of pure didymium oxide by acids so altered the most important absorption ray furnished in the spectrum of that earth as to destroy its characteristics.[3]

Up to the present time the following earths have been found in samarskite. I give the list as made out by Delafontaine, with the exception of mosandrum, which he does not recognize:

Yttria,	Thoria,
Erbia,	Oxide didymium,
Terbia,	Oxide cerium,
Philippia,	Mosandria.
Decipia,	

The proportion of each of these earths in the 14 per cent. of earths it is impossible to state. As regards the thoria it is about 0.50 of the mineral. The oxides of cerium and didymium exist only in traces.

The method of separating most of these earths is by fractional precipitation with oxalic acid, or by some alkali as employed by myself. Operating with the ignited nitrate is used in other instances, but in whatever manner the separation is attempted it is

[1] Comptes rendus, 1877, **85**, 634. [2] *Ibid.* 1878, **86**, 422. [3] *Ibid.* 1878, **86**.

attended with difficulty and greatly reduces the quantity of the residuary oxide which is sought for.

It is the insoluble precipitate D that furnishes the difficult problem of quantitative analytical chemistry, and several earths of yet undefined character have been more or less perfectly separated. I will give some of my own labors in that direction.

Many interesting results have been worked out by Marignac, of Geneva, and Delafontaine, of Chicago; but the slow, tedious processes that have to be employed will delay those labors very much.

The method by which I made some imperfect operations on the oxalate C is as follows: The powder is dried, ignited and weighed. It has a pale yellow color, and consists of several earthy oxides. It is completely soluble in dilute or strong nitric acid. The solution of it in the acid is evaporated to the consistency of thick syrup, thus driving off nearly all the free acid. To this syrupy mass, before it solidifies,[1] about 50 cc. of a concentrated solution of sulphate of potassium or sodium (lately I have used the sodium salt altogether), and mixed into the mass. It gives at first a clear solution. To this is added three or four grams of small crystals of the sulphates, the whole stirred frequently and allowed to stand for 24 hours. A precipitate soon begins to form, and at the end of the time is quite abundant. It is now thrown into a filter and thoroughly washed with a concentrated solution of potassium or sodium sulphate, but at no time will the filtrates be entirely free from a trace of the insoluble double sulphate. This precipitate is called D. The filtrate is supposed to contain yttria and erbia. To it is added oxalic acid or ammonium oxalate, the precipitated oxalate burnt, redissolved and reprecipitated[2] by the oxalate, then burnt, and after very thorough ignition, weighed. This oxide is then dissolved in dilute sulphuric acid, evaporated carefully to dryness, and heated nearly to red heat, until its weight is constant. This is noted, and from the weight of the oxide and that of its sulphate, the relative proportion of yttria and erbia is estimated by the formula of Bahn and Bunsen:

$$x = 4.9806A - 2.4540B.$$

x = the erbia contained in A; the oxides, which give B, the

[1] We are supposed to be operating with one or two grams of the mineral.

[2] This second precipitation is always necessary when we are analysing these earths and the first solution contains potash and soda.

sulphates.[1] The first precipitate by the sodium sulphate, washed with a solution of the same, is dissolved in hydrochloric acid, and first precipitated as oxalates, then changed into oxides by ignition. It is in this oxide that I searched for mosandrum by repeated precipitation with sodium sulphate and reconversion into oxides, when I obtained an oxide as dark as cerium oxide, dissolved in minute quantity in sodium sulphate and perfectly soluble in very dilute nitric acid, after 30 minutes' contact.

The insoluble double sulphates D precipitated from the solution of the earths may contain any or all of the other cerium oxides and thoria. This is dissolved in water containing a little chlorhydric acid, by the application of heat; the solution is then nearly neutralized by ammonia and precipitated by oxalic acid or oxalate of ammonia, the precipitate is burnt, redissolved in nitric acid and reprecipitated by the oxalate, which is well burnt and weighed.

This was originally supposed to be the cerium group of earths, but when rubbed up with a little water it is completely dissolved[2] in dilute nitric acid (1 acid to 100 water), in from 15 to 30 minutes, showing the absence of cerium oxide, or if present, only to the extent of a mere trace.

To test this fact still farther, I precipitated the earth from its nitric acid solution by caustic soda, adding just enough to make the solution alkaline, then added 3 to 4 grams of caustic soda, and adding water enough to make the mixture 50 cc., it is quite thick from the gelatinous precipitate. A stream of chlorine gas is now passed slowly through the mixture for 2 or 3 hours, in the manner recommended by M. Mosander for separating cerium oxide from its associated earths. But none of the indications of color peculiar to cerium oxide are manifested, but all the oxides are taken into solution except a small quantity of a white gelatinous precipitate. This precipitate was collected on a filter and washed, detached from the filter and dissolved by means of a few drops of sulphuric acid, evaporated to dryness, heated to drive off the excess of acid, and, when dissolved in a little cold water and examined, was found to be thoria.[3] It was afterwards precipitated

[1] In the use of this method of operation it was supposed that cerium oxide and yttria could be easily separated from each other by the bisulphate of potassium and sodium, and the oxides remaining in solution were yttria and erbia, but more recent research has shown its defective character, and it is no longer adapted to furnish any good method.

[2] This is based on the supposition that there is no other oxide present.

[3] The cold solution when heated was changed into a mass of the delicate silky crystals so remarkably characteristic of thoria.

by ammonium oxalate, burnt and weighed, and represented 0.80 per cent. This is a new and valuable method of separating thoria, which will be treated of in another part of this paper.

The fact of the absence of cerium oxide led to a thorough examination of the D precipitate; for the Russian variety of samarskite contains cerium. But to do this I had to make the study upon a much larger quantity of the earths than that obtained from 5 grams of the mineral, which contain only about 4 per cent. of the D oxides, so that what follows is based on the use of ample material obtained from several kilograms of the mineral.

In this large operation I did not use platinum vessels for the first treatment, but lead vessels, the decomposing vessels being of the capacity of four litres, and capable of working more than one kilogram at a time, and the mineral was sufficiently divided by passing it through a wire sieve with ½ mm. meshes (less than 30 minutes being required to prepare a kilogram for the action of the fluorhydric acid). The mineral is placed in the lead capsule and 750 cc. of water poured upon it, then one kilogram of fuming fluorhydric acid is added by degrees, and the mixture stirred with a lead rod until the violence of the action ceases. Then a second kilogram of acid is added and stirred in. The capsule is now placed on a water-bath and heated, with occasional stirring, for two or three hours, when the action is complete, and we proceed as already described with the 5 grams.

When the insoluble fluorides of the earths are obtained I find the following the best way of changing them to oxalates. 250 grams of the dry fluorides rubbed up in a mortar and placed in a platinum capsule, and then 250 cc. of concentrated sulphuric acid are added without water, the mixture stirred and heated over the flame until nearly dry, and after cooling, dissolving in water and uranium oxide farther oxidized by nitric acid. After filtration the whole is diluted to about 5 litres, boiled by a current of steam, nearly neutralized and then precipitated by 225 grams oxalic acid dissolved in one litre of water. The oxalates thus obtained are operated with as already described for the separation of yttria, using either potassium sulphate or sodium sulphate. The latter has certain advantages in large operations. The thoria of the earths is with that part which is difficultly soluble in sodium sulphate.

Separation of Thoria.

The separation of this earth from the others with which it is usually associated is attended with more or less difficulty and uncertainty. These earths are of the cerium group, for the concentrated solution of potassium sulphate precipitates the thoria along with these earths. One of the best methods is considered to be that by sodium hyposulphite, but the use of it did not enable me to decide upon the presence of thoria when I made the examination for my mineralogical paper on the "Columbic acid minerals of the United States,"[1] while the method about to be described makes it easy of detection and quantitative separation; so much so that I am satisfied that by means of it the metal thorium will be found to be more generally diffused than it has been supposed to be.

If thoria be precipitated from a solution of any of its salts by the fixed alkalies, and the gelatinous precipitate added to a little water containing four or five times its weight of caustic potash or soda, and a current of chlorine gas passed through it for any length of time, none of the thoria will be taken into solution; and if the other earths usually associated with thoria be present, the same result will take place as regards the thoria, but all the other earths will be dissolved with the exception of the cerium oxide. These facts have been fully verified by a special set of experiments. The thoria in the samarskite was estimated in this way,[2] and no analytical result could be more satisfactory, sufficient care being taken to pass chlorine gas through the solution long after it is supposed to be saturated. Two or three hours is not too long where ½ to 1 gram of the mixed oxides is operated with.

Separation of the thoria from the mixed earths by ammonia.—When thoria has to be separated from a large quantity of its associate earths, the chlorine method is long, and the insoluble part has to be separated and treated two or three times before complete separation is accomplished. I accomplished this by an excellent method, but one not intended to furnish quantitative results like the chlorine method.

Using, say fifty grams of the earths separated by the potassium or sodium sulphate, dissolve it in nitric acid somewhat diluted, and concentrate over a water-bath, add the contents of the capsule to about three litres of water, boil by a current of steam or otherwise,

[1] Am. Journal of Science, **13**, May, 1877.

[2] As already described where treating of the absence of cerium oxide in the samarskite.

and, when in a state of ebullition, neutralize by ammonia until only a few flakes remain undissolved; then add by degrees an ammonia solution of known strength and just sufficient to precipitate six or eight grams of the oxides,[1] the solution being made to boil violently during the operation. This ebullition is continued for about five minutes. A bulky gelatinous precipitate will be formed which contains all the thoria and a little of the other oxides. This is thrown on a filter and washed. This takes place very slowly. The gelatinous precipitate is dissolved in a dilute solution of sulphuric acid, evaporated to dryness, excess of acid driven off, redissolved in cold water. By boiling and evaporation it separates in its well-known form, which, when hot, is separated from the mother-liquor. The sulphate of thorium thus obtained is not perfectly pure, but if wanted for chemical investigations it can be purified by the usual method. This separation clearly arises from the fact that the thoria is less basic than the other earths.

The filtrate from the gelatinous precipitate is treated with oxalic acid, and the precipitated oxalate dried and ignited, giving a salmon yellow oxide that is further examined by processes to be described. The fact that these earths have only a mere trace of thoria remaining in them is established by the fact that, when one gram of them is treated by the chlorine test for thoria already described, all the oxides are completely dissolved except 4 milligrams. I then recommend this method as one likely to prove useful for the purification of large quantities of the earths containing thoria in small quantity.

The earth from the thoria is of a salmon yellow color, its oxalate burns readily, and all tests were applied to discover lanthanum oxide, and only a very doubtful evidence of its presence was obtained. So that, of the three cerium metals, only didymium oxide remained to look for. A nitric acid solution gave the very well known spectroscopic bands of that metal, but it was impossible to separate it by a chemical process. But by making use of the spectroscope I think I have approximated to the proportion mixed with the oxides in the following manner:

Quantitative Estimate of Didymium Oxide by its Absorption Bands.

Make solutions of the oxide of didymium of known strength, and place the solutions in tubes of uniform diameter. Vials of thin glass

[1] In the present instance I have calculated the amount on the basis of an atomic weight of the oxides of 116 (O=16).

1½ cm. diameter were used. Then take the oxides to be tested, dissolving a known quantity of the oxides in a solution of nitric acid, placing in a tube of the same size as those containing the didymium salt of known strength, compare the solution in the tubes before the spectroscope with the different didymium tubes, and it will be soon seen which one of these latter gives bands corresponding in intensity with the didymium bands in the solution of oxides that are tested; and knowing the exact proportions of oxide in the didymium tube, a good approximate result may be obtained.

I am now making an apparatus, using only one solution of didymium and simply varying at pleasure the thickness of the solution. In this way I estimate that the mixed earthy oxides of samarskite contain less than 0.25 of didymium. As regards the principal portion of the earth separated from the yttria, I consider it as an oxide, or oxide of a new earth, for I cannot reconcile my mind to the idea that it is principally terbia. One of the earths present I call mosandrum, and M. Delafontaine has separated two, phillipium and decipium.

Owing to the fact of bodily indisposition I have not been able to continue my researches on these earths.

For the complete quantitative analysis of samarskite, reference is made to labors previously made by myself and others[1], with this difference that in the earthy oxides there is 0.50 per cent. of thoria, and the cerium referred to is not that oxide, but other mixed oxides.

ON THE ACTION OF AROMATIC OXY-ACIDS ON PHENOLS.

By Arthur Michael.

The investigation of the action of alkalis on naturally occurring organic compounds has shown that a considerable number of these bodies undergo in this operation a decomposition into phenols and aromatic oxy-acids. These compounds are distinguished by the greater or less ease with which they undergo this decomposition.

[1] Am. Jour. of Science, May, 1877.

While some of them only require to be heated with dilute aqueous alkaline solutions, others are not decomposed unless they are treated with alkalis at a high temperature. The easily decomposable compounds are probably compound ethers of phenols and oxyacids; as maclurin, which may be considered the phloroglucinether of protocatechuic acid; or phloretin, the phloroglucinether of phloretic acid. The second class consists largely of compounds which are more or less complicated derivatives of aromatic oxyketones. As examples of this class may be mentioned euxanthone— $C_6H_3\begin{cases}OH\\ \\ CO\end{cases}O—C_6H_3OH$—or gentianin, which is probably a methylether of the compound $C_6H_3\begin{cases}OH\\ \\ CO\end{cases}O—C_6H_3(OH)_2$.

Several compounds showing an analogous behavior towards alkalis have been obtained synthetically. Paradioxydiphenylketone — $C_6H_4<\begin{matrix}OH\\ CO\end{matrix}>C_6H_4OH$—is formed (1) By the action of water at a high temperature on rosaniline[1] or aurine;[2] (2) By the action of potassium hydrate on phenol-phthalein;[3] (3) From diphenylketone by means of the α-dinitro and diamido derivatives.[4] An isomeride, yielding also phenol and p-oxybenzoic acid on fluxing, was obtained in a similar manner from β-dinitrodiphenylketone.[4] The compound $C_6H_4<\begin{matrix}O\\ CO\end{matrix}>C_6H_4$, which may be considered as an ether of the unknown diortho dioxydiphenylketone, has been obtained in the following reactions: by the oxidation of $C_6H_4<\begin{matrix}O\\ CH_2\end{matrix}>C_6H_4$;[5] by the action of phosphorus oxychloride on disodiumsalicylate;[6] among the products obtained by the distillation of o-chlorobenzoic acid, or a mixture of phenylphosphate and sodiumsalicylate;[6] by passing phenol over heated lead oxide,[7] and finally by the oxidation of the compound obtained by heating euxanthone with zinc dust.[8] An analogous compound has been obtained by Buchka by the action of potassium hydrate on gallein.[9]

The present investigation was undertaken in the hope of obtaining some of the natural products synthetically. The results

[1] Liebermann, Ber. 1872, 951, 1878, 1435.
[2] Baeyer and Burkhardt, Annalen, **202**, 126.
[3] Merz and Weith, Ber. 1881, 191.
[4] Behr and Dorp, Ber. 1874, 398.
[5] Annalen, **209**, 270.
[6] Caro and Graebe, *Ibid.* 1878, 1348.
[7] Staedel and Sauer, Ber. 1878, 1747.
[8] Richter, J. pr. Chem. [2] **23**, 349.
[9] Wichelhaus and Salzmann, Ber. 1877, 1397.

described in the present paper will prove that by the direct action of aromatic oxy-acids on phenols, or by the aid of suitable dehydrating agents on such mixtures, bodies belonging to the above class of compounds may be obtained.

Action of Tin tetrachloride on a mixture of Phenol and Salicylic Acid.

A mixture of phenol and salicylic acid was heated both in open vessels and in sealed tubes at various temperatures, without any reaction ensuing. The addition of dehydrating agents to the mixture effects a reaction in an open vessel at a moderate temperature. Zinc chloride and tin tetrachloride have been used, the latter reagent giving the most satisfactory results. The following proportions were found to give the best yield: To 50 grams of phenol and an equal weight of salicylic acid 40 grams of tin tetrachloride were added, and the mixture heated in an oil-bath for twelve to fourteen hours at 115°–120°, finally for several hours at 125°. The salicylic acid soon dissolved in the mixture of phenol and tin tetrachloride, forming at first a colorless liquid which on further heating took a yellow color, growing in intensity of color as the reaction proceeded. After heating several hours, beautiful yellow needles were deposited from the liquid, and continued to separate until the reaction ceased. The melted flux was then poured into a large quantity of boiling water, and the insoluble residue treated with steam to free it from undecomposed phenol. The crystalline product was dissolved in warm alcohol, and the solution treated with hydrogen sulphide to free it from tin. The filtrate, after being concentrated by evaporation, yielded crystals, which were purified by treatment with bone-black and repeated crystallization from alcohol. This method of purification was later given up for the following more simple treatment. The flux, which contains a double compound of the new body with tin tetrachloride, phenol and salicylic acid, was freed from phenol by treating with steam, and the residue boiled with a large excess of a concentrated solution of sodium carbonate. The filtrate, which was found to contain no tin, was treated with carbon dioxide until complete precipitation ensued. The precipitate was dissolved in sodium hydrate, and again treated with carbon dioxide. Towards the end of the precipitation it was noticed that long white needles were deposited in place of a reddish crystalline powder. At this point the origi-

nally dark liquid had become light brown, the product was filtered, and the filtrate then treated with carbon dioxide until complete precipitation took place. The red precipitate contained a small quantity of the white needles; these were separated by extracting several times with a small amount of boiling water. The residue was obtained in a pure state by two crystallizations from benzene and one from alcohol, after treatment with animal charcoal.

Zinc chloride, in place of tin tetrachloride as dehydrating agent, gave a very small yield of the new substance. A mixture of equal weights of phenol, salicylic acid and fused powdered zinc chloride formed on heating a homogeneous liquid, which soon took a dark yellow color. The mixture was heated for six hours, and the flux then treated with sodium carbonate and carbon dioxide as above described.

An analysis of the substance gave the following numbers: 0.2466 gram, dried at 100°, gave 0.6596 gram of CO_2 and 0.1085 gram of H_2O.

	Theory for $C_{13}H_{10}O_2$.	Found.
C	72.89	72.91
H	4.67	4.88
O	22.44	22.21

The hot aqueous solution of the substance deposits, on cooling, large, glittering, pale-yellow plates; the hot alcoholic solution, small well-defined plates. A solution in benzene, saturated at its boiling point, yields on cooling pyramids with symmetrically truncated end-faces. The substance melts at 143–144°. It is almost insoluble in cold, moderately soluble in hot water. Alcohol and benzene dissolve it readily in the hot, sparingly in the cold. Alkalis dissolve it with ease in the cold to form the corresponding phenylate. This solution treated with carbonic acid yields a precipitate of the original compound. In the preparation of the substance attention was called to the separation of yellow needles from the melted flux. These needles are a double compound of the substance with tin tetrachloride, and are obtained when the two substances are brought together. They are readily soluble in water and alcohol. The analysis and investigation of the properties of the compound show that it is a dioxybenzophenone. To distinguish it from the isomeric paradioxybenzophenone I propose the name salicylphenol.[1] The substance is formed by the elimina-

[1] The unknown phenolether of salicylic acid should be called phenylsalicylate or salicylphenolether.

tion of a molecule of water from a molecule of salicylic acid and one of phenol, a reaction represented by the equation:

$$C_6H_4{}^{OH}_{COOH} + C_6H_5OH = C_6H_4{<}^{OH}_{CO} - C_6H_4.OH + H_2O$$

Salicylphenol forms a series of well-defined derivatives, in which the hydrogen of the hydroxyl groups are replaced by metals. To obtain the sodium derivative an excess of the powdered substance was allowed to stand with dilute aqueous sodium hydrate for several days, and the undissolved substance separated by filtration. The filtrate evaporated to incipient dryness solidified to stellular groups of navicular-shaped needles, which are very soluble in water and alcohol.

0.4580 gram Na compound, dried at 100°, gave 0.2486 gram Na_2SO_4.

	Theory for $C_6H_4{}^{ONa}_{CO}C_6H_4ONa$.	Found.
Na_2	17.83	17.60

The silver compound was obtained as a bright yellow precipitate by addition of silver nitrate to an aqueous solution of the sodium derivative. It is sparingly soluble in water, and contains one molecule of water of crystallization.

0.6904 gram silver compound, air-dried, lost 0.0272 gram H_2O when dried at 100°.

	Theory.	Found.
H_2O	4.01	3.79

I. 0.4483 gram Ag compound, dried at 100°, gave 0.206 gram Ag.

II. 0.3863 gram Ag compound, dried at 100°, gave 0.179 gram Ag.

	Theory for $C_6H_4{}^{OAg}_{CO}C_6H_4OAg$.	Found.	
		I.	II.
Ag_2	46.55	46.00	46.33

The mercuric salt separated on addition of a solution of mercury dichloride to an aqueous solution of disodiumsalicylphenylate as a reddish yellow precipitate. It is sparingly soluble in hot water, and is deposited from this solution on cooling as navicular-shaped needles. When it is boiled with a small quantity of water the color of the salt changes to red. The addition of iron trichloride to a solution of the sodium derivative gave a brown precipitate.

This is moderately soluble in water, and is deposited from the hot aqueous solution on cooling as fern-shaped crystals.

The copper derivative formed a greenish-yellow precipitate, and is insoluble in hot water. By boiling with water the amorphous precipitate changed into crystalline groups of rhombic plates.

A lead derivative was obtained as a yellow amorphous precipitate, which melted under boiling water. The aqueous solution of disodiumsalicylphenylate was not precipitated by addition of barium nor calcium chlorides.

The second substance formed by the action of tin tetrachloride on salicylic acid and phenol is obtained by precipitating the filtrate from salicylphenol with carbonic or hydrochloric acid. The substance was purified by repeated crystallization from water. An analysis proved that the substance has the same empirical formula as salicylphenol. 0.2071 gram substance, dried at 100°, gave 0.5516 gram CO_2 and 0.930 gram of H_2O.

	Theory for $C_{13}H_{10}O_3$.	Found.
C	72.89	72.68
H	4.67	4.97

The substance separates from hot water, in which it is more soluble than salicylphenol, in plates or needles, from alcohol in large plates. It melts at 205.5°–206.5°. Boiled with acetic anhydride and sodium acetate it yields an acetyl derivative. This crystallizes in long needles, melting at 148°. A comparison of these properties with those of paradioxybenzophenone[1] shows that the compounds are identical. The formation of this compound was due to the presence of a small amount of paraoxybenzoic acid in the commercial salicylic acid used.[2] This view was confirmed by the direct synthesis of paradioxybenzophenone from paraoxybenzoic acid and phenol. These substances heated with tin tetrachloride for ten hours, and the product treated as described for the preparation of salicylphenol, yielded paradioxybenzophenone.

Action of Acetic-anhydride on Salicylphenol.

Acetic anhydride converts salicylphenol readily into the diacetyl derivative. A mixture in the proportion of one mol. salicylphenol, three mols. acetic anhydride, and one mol. fused sodium acetate was

[1] Staedel and Gail, Annalen, **194**, 334. Baeyer and Burkhardt, *Ibid.* **202**, 129.
[2] Ost, Journ. p. Chem. [2] **20**, 208.

heated for several hours in boiling water. The product was poured in cold water. The insoluble oil soon solidified to a crystalline mass, which was purified by several crystallizations from dilute alcohol.

An analysis of the substance, dried in vacuum over H_2SO_4, gave the following numbers:

0.2150 gram substance gave 0.5417 gram CO_2 and 0.0965 gram H_2O.

	Theory for $C_6H_4{}^{OOCCH_3}_{COC_6H_4OOCCH_3}$.	Found.
C	68.47	68.71
H	4.69	4.98

Diacetsalicylphenol separates from hot water in long, concentrically grouped white needles, that melt at 84°–85°. They are sparingly soluble in cold, moderately soluble in hot water. In cold alcohol and benzene moderately soluble, they are readily soluble in these solvents when warm. An aqueous solution of potassium hydrate does not dissolve the compound in the cold; when heated it is gradually dissolved, forming a yellow solution. Carbonic acid precipitated salicylphenol from this solution.

Action of Potassium and Sodium Hydrates on Salicylphenol.

The formation of salicylphenol from salicylic acid shows that the relation of one of the hydroxyl groups to the carbonyl group is that of ortho-derivatives. The products obtained by fluxing salicylphenol with alkalis make it probable that the relation of the second hydroxyl group is that of para-derivatives.

Salicylphenol was heated with three times its weight of potassium hydrate and a small quantity of water until the addition of hydrochloric acid to a portion of the flux dissolved in water ceased to give a precipitate. The yellow color of the flux gradually changed to a light brown. The flux was dissolved in water, acidified with dilute sulphuric acid, filtered, and the filtrate treated with steam. The distillate contained phenol. This was shown by isolation of the product and comparison of its properties with those of phenol. Tribromphenol (melting point 97°) was immediately precipitated on addition of bromine to the distillate. The liquid remaining in the flask after treatment with steam was extracted several times with ether, and the extracts evaporated to dryness. The white crystalline substance which remained was crystallized several

times from water, and then showed all the properties of paraoxybenzoic acid. The fact that a number of ortho-benzene derivatives have been shown to pass over into para-compounds by fluxing with potassium hydrate made it desirable that the experiment should be repeated, using sodium instead of potassium hydrate. The experiment showed that the same products are formed in the action of sodium hydrate on salicylphenol. Salicylphenol is therefore an ortho-para derivative of benzophenone. The action of alkalis is represented by the equation:

$$C_6H_4\overset{OH}{\underset{CO}{}}—C_6H_4OH+3KOH$$
$$=p\text{-}C_6H_4OKCOOK+C_6H_5OK+2H_2O.$$

The decomposition of orthoparadioxybenzophenone into paraoxybenzoic acid and phenol is of interest as showing the effect of the hydroxyl groups upon the affinity of the carbonyl group to the phenylene radical. It indicates that the ortho-hydroxyl group loosens the affinity to a greater extent than the para-hydroxyl group.

Action of nascent Hydrogen on Salicylphenol.

The carbonyl group of salicylphenol is not reduced by subjecting the compound to the action of zinc and hydrochloric acid or potassium hydrate and zinc dust. The reduction may be easily effected by allowing sodium amalgam to act on an alkaline solution of the substance. Sodium amalgam (2 per cent. Na) was gradually added to a solution of salicylphenol in potassium hydrate, and the reaction continued until the liquid became perfectly colorless. The alkaline liquid was then decanted from the mercury, and carbon dioxide passed through it until complete precipitation of the reduction product. All attempts to obtain the white amorphous precipitate in a crystalline form were without success. For purification it was dissolved in potassium hydrate, and again precipitated by treatment with carbon dioxide.

An analysis of the substance, dried over sulphuric acid *in vacuo*, gave the following numbers:

0.2017 gram substance gave 0.5323 gram CO_2 and 0.0987 gram H_2O.

	Theory for $C_{13}H_{12}O_3$.	Found.
C	72.89	72.68
H	4.67	4.97

The compound was formed by the addition of two hydrogen atoms to salicylphenol, and is o-p-dioxydiphenylcarbinol:

$$C_6H_4OHCOC_6H_4OH + H_2 = C_6H_4OHCHOHC_6H_4OH.$$

Dioxydiphenylcarbinol is a white amorphous powder, which, when rubbed with an insulator, becomes strongly electric. It is insoluble in cold, somewhat soluble in hot water. Heated with a small quantity of boiling water the substance melts. Cold alcohol dissolves it readily; the alcoholic solution leaves an oil on evaporation of the alcohol which did not solidify on standing. In alkalis it is readily soluble, forming the corresponding phenylates. O-p-dioxydiphenylcarbinol, like diparadioxydiphenylcarbinol,[1] undergoes a very striking change when heated with mineral acids. It is converted into a dark violet-blue color. The reaction is extremely delicate; several drops of dilute hydrochloric acid suffice to convert a considerable quantity of the carbinol into the blue color. Neither the color nor its acetyl derivative could be obtained in a crystalline state. Distilled over zinc dust in a current of hydrogen it gave a small yield of a crystalline substance.

Action of Salicylic Acid on Resorcin.

While the formation of salicylphenol takes place only when salicylic acid and phenol are heated in presence of a dehydrating agent, it was found that an oxyketone was formed by heating a mixture of salicylic acid and resorcin, and that the same mixture heated with a dehydrating agent gave a different result.

To investigate the action of salicylic acid on resorcin, a mixture of 8 parts of the acid and 15 parts of resorcin was put in a long-necked flask, and heated in an oil-bath at 195°–200° for about 15 hours. It is advisable to keep the temperature of the bath at 195° for the first five hours, and then to raise it to 200°. The mixture soon took a dark brown color, a sublimate of salicylic acid was formed and the deposition of water and phenol took place on the sides of the flask. The hot flux, which becomes quite hard on cooling, was poured into cold water slightly acidulated with hydrochloric acid, and allowed to stand for 12 hours. The insoluble crystalline residue was extracted with a dilute solution of sodium carbonate—a saturated solution of the salt diluted with six parts of

[1] Baeyer and Burkhardt, Annalen **202**, 132.

water—which dissolves a brown amorphous substance and undecomposed salicylic acid. The brown-yellow residue was dissolved in alcohol, boiled several hours with animal charcoal, some water added to the filtrate and the solution boiled until it became turbid. On cooling, part of the substance separated as an oil, which solidified on cooling; the greater part crystallized out as large yellowish-red scales after the solution had cooled. To obtain the substance pure it was extracted with ligroin containing a small amount of chloroform, which left a slight impurity undissolved, and crystallized twice from this solvent.

On analysis the substance gave the following numbers:

0.2623 gram of substance gave 0.6522 gram of CO_2 and 0.1085 gram of H_2O.

	Theory for $C_{13}H_{10}O_4$.	Found.
C	67.82	67.79
H	4.35	4.59

From hot dilute alcohol it is deposited on cooling as glistening yellow scales; from ligroin as arborescent, pale yellow, crystalline groups. It is insoluble in cold, very slightly soluble in hot water. Alcohol and benzene dissolve it readily. Treated with alkalis in the cold it dissolves to form a yellow solution. A dilute solution of potassium carbonate dissolves it slowly. From these solutions carbonic acid precipitates the original substance. Heated with water it volatilizes slowly, giving the steam a peculiar aromatic odor. The crystals melt at 133–134°; the melted substance solidifies at 116–117°. Acetic anhydride converts the compound into an acetyl derivative. This formed an oil, which solidified partially after long standing, but the solid compound was not obtained in sufficiently pure state for analysis. A solution of the substance in concentrated aqueous potassium hydrate may be boiled without decomposing the ketone. It is easily decomposed when fluxed with alkalis. Heated with caustic potash and a small amount of water for several minutes, the presence of salicylic acid and resorcin was proved in the flux by their isolation. An alkaline solution of the substance treated with sodium amalgam gave a product with properties similar to those of dioxydiphenylcarbinol. The white reduction product gave a green coloring matter when heated with dilute acids.

The above described properties of the substance show that it is a trioxybenzophenone or salicylresorcin. This view is corrobo-

rated by its behavior towards zinc chloride, which will be described further on. The yield of salicylresorcin obtained in the above process was very small.

$$C_6H_4OHCOOH + C_6H_4(OH)_2 = C_6H_4(OH)COC_6H_3(OH)_2 + H_2O.$$

Action of Zinc Chloride on a mixture of Resorcin and Salicylic Acid.

It has already been mentioned that the action of salicylic acid on resorcin, in the presence of zinc chloride, gives rise to a new product. The following directions were found to give the best result, although the yield obtained was but small. Twenty grams of resorcin and an equal weight of salicylic acid were melted, and about fifteen grams of fused, pulverized zinc chloride added to the clear flux. The flux soon took a yellow, then a yellowish-brown color, which increased in intensity with continued heating. After the mixture had been kept melted for about two hours, it was poured into ½ liter of warm water. The dark residue may be purified by crystallizing once from glacial acetic acid and then three times from alcohol. A more advantageous method of purification is founded on the insolubility of the sodium derivative of the new compound. The flux, after treatment with warm water, was extracted several times in the cold with an aqueous solution of dilute sodium hydrate. The straw-colored residue was then treated with hydrochloric acid, filtered, and the insoluble portion crystallized twice from alcohol.

The substance does not contain water of crystallization.

0.356 gram of air-dried substance weighed 0.355 gram when dried at 100°.

0.261 gram of substance, dried at 100°, gave 0.7051 gram of CO_2 and 0.0872 gram of H_2O:

	Theory for $C_{13}H_{10}O_3$.	Found.
C	73.58	73.68
H	3.77	3.71

The formula $C_{13}H_{10}O_3$ is that of salicylresorcin less one molecule of water. That the new compound stands in the relation of that of an anhydride to salicylresorcin will be shown below. I propose the name salicylresorcin ether, as indicating this relationship. Its

formation from salicylic acid and resorcin may be represented as follows:

$$C_6H_4OHCOOH + C_6H_4(OH)_2 = C_6H_4<\begin{matrix}O\\CO\end{matrix}>C_6H_3OH + 2H_2O.$$

Salicylresorcin ether crystallizes from alcohol in long, bright yellow needles. It is insoluble in cold, but sparingly in hot water. Cold alkaline solutions convert it into yellow, slightly soluble needles, consisting of the corresponding phenylate. It melts at 146–147°.

Salicylresorcin ether can be obtained from salicylresorcin by the action of zinc chloride. The latter substance and an equal weight of zinc chloride were kept melted for about ten minutes. The flux was treated in the same manner as the flux obtained in the preparation of salicylresorcin ether and yielded this compound:

$$C_6H_4(OH)COC_6H_3(OH)_2 = C_6H_4<\begin{matrix}O\\CO\end{matrix}>C_6H_3OH + H_2O$$

The inverse reaction, to obtain salicylresorcin from its ether, was not realized. Fused with sodium and potassium hydrates it gave the same decomposition products as salicylresorcin, *i. e.* salicylic acid and resorcin.

Salicylresorcin ether forms a series of metallic derivatives, characterized by their insolubility in water. This property is even shown by the alkali derivatives, which are among the least soluble products containing these metals. Only the sodium derivatives have been examined, but the results already obtained will be found to present some interest.

A boiling saturated solution of salicylresorcin ether (one mol.) poured into a solution of sodiumethyloxide (three mol.) in 80 per cent. alcohol gave momentarily a clear yellow solution. This soon solidified to a mass of lemon-colored, long needles, which were washed with a small quantity of absolute alcohol, then well pressed between bibulous paper and dried at 110°. On analysis the following results were obtained:

I. 0.4990 gram of substance, dried at 110°, gave 0.2555 gram of Na_2SO_4.

II. 0.2945 gram of substance, dried at 110°, gave 0.1556 gram of Na_2SO_4.

	Theory for $C_{13}O_3H_7Na$, NaOH	Found. I.	II.
Na	16.76	16.57	17.10

This disodium derivative treated with water, or a large amount of alcohol, gives products containing less sodium; a substance having a constant composition could not be obtained. It was found that by repeated treatment with cold water the complete decomposition of the disodium compound into salicylresorcin ether and sodium hydrate could be effected. The disodium compound is stable in the presence of strong aqueous or alcoholic sodium hydrate. An alcoholic solution of the ether poured into an excess of aqueous sodium hydrate gave a precipitate of pale yellow needles. This consisted largely of the mono-sodium derivative, as the following analysis showed:

0.4568 gram of substance, dried at 100°, gave 0.1653 gram of Na_2SO_4.

	Theory for $C_{13}O_3H_7Na$.	Found.
Na	9.83	11.72

Salicylresorcin ether treated with potassium and ammonium hydrates gave derivatives with properties similar to those of the disodium compound.

Relative to the constitution of the disodium compound it might be supposed that salicylresorcin ether adds sodium hydrate, forming $C_6H_4\langle^{ONa}_{CO}\rangle—C_6H_3{}^{OH}_{ONa}$, a derivative of salicylresorcin. This view cannot be upheld, as salicylresorcin is readily soluble in sodium hydrate, and no precipitate is formed by the addition of a large excess of that reagent to the solution. The fact that the disodium compound when treated with acids yields the ether, while salicylresorcin can only be converted into the ether by means of a strong dehydrating agent, also shows it to be a derivative of the ether. It is not unlikely that the carbonyl group of the ether plays a part in the formation of the disodium compound. There are facts known which seem to imply the capability of the carbonyl group in certain cases of uniting with the alkaline hydrates to form derivatives of the types $\left(=C^{OM}_{OH}\right)$ and $=C^{OM.}_{OM}$[1] From this point of view the

[1] The metallic derivatives of coumarin (Williamson, Chem. Soc. Jour. **28**, 850) probably belong to this class of compounds. The disodium compound would have the constitution $C_6H_4\langle^{O\ \ —C\langle^{ONa}}_{CH—CH}{}^{}_{ONa}$. These compounds have lately been made the subject of some interesting experiments by W. H. Perkin (Chem. Soc. Jour. 1877, 388; 1881, 409 and 554). This chemist obtained by treating equal molecules of the disodium compound and methyliodide the sodium salt of an acid, which is isomeric with the methylcumaric acid obtained by the action

constitution of disodium salicylether may be represented by the formula $C_6H_4<\begin{matrix}O\\COH\\ONa\end{matrix}>C_6H_4ONa$. The action of methyliodide on the sodium compound yields methyl substitution derivatives, the examination of which will probably help to a better understanding of the constitution of this class of compounds.

Action of Acetic Anhydride on Salicylresorcin-ether.

To prepare the acetyl derivative of salicylresorcin ether, equal parts of this substance and fused sodium acetate, and three parts of acetic anhydride were heated for three hours at 110°. The contents of the flask poured into cold water yielded an oil, which soon solidified. The crystalline mass was crystallized several times from alcohol. It separates from hot alcohol as white, prismatic needles, which melt at 167°-168°. The crystals are very slightly soluble in cold or hot water; easily in hot, sparingly in cold alcohol. Heated

of methylsalicylaldehyde on acetic anhydride. It was also noticed that the first acid (α-acid) goes over on heating into the second acid (β-acid), and that this property extends to the ethers of the α-acid. A comparison of the physical properties of the corresponding derivatives of the two acids showed that the boiling points, densities and magnetic rotary power of the α-derivatives are lower than those of the β-series. For these facts, and that "this isomerism cannot be explained by any ordinary kind of chemical constitutional formula we have at present," Perkin offers the following explanation:

"These facts would seem to indicate that in the α-compounds the groups, or some of them, contained in the molecules are farther apart than in the β-compounds."

It does not seem to me that our knowledge of this interesting case of isomerism has been at all increased by this hypothesis. To take an illustration, let us suppose that the conversion of methylaniline chlorhydrate into toluidine chlorhydrate by heat had been discovered when their isomerism could not be explained by "any ordinary kind of chemical constitutional formula," and it was known that p-toluidine has a higher boiling point and greater density than methylaniline, would the hypothesis that the "groups, or some of them," in the molecule of methylaniline are farther apart than in p-toluidine have been a satisfactory explanation? If I rightly understand what Perkin means by "any ordinary kind of chemical constitutional formula," I think this chemist will find that the isomerism of the α and β-acids may be easily represented by constitutional formulæ. The action of methyliodide on disodium coumarin gives the sodium derivative of $C_6H_4<\begin{matrix}O-C<\begin{matrix}OH\\OCH_3\end{matrix}\\CH-CH\end{matrix}$, a compound which is a lactone derivative of mono-methylorthocoumaric acid, and is isomeric with $C_6H_4<\begin{matrix}O-CH_3\\CH-CH-COOH\end{matrix}$. The acid ethers of the ortho-organic acids are as yet but little known. There is however a class of compounds discovered by Nencki and Sieber (Journ. pkt. Chem. [2], **23**, 147), which undoubtedly belong to this group. Thus the compound obtained by the action of zinc chloride on acetic acid and resorcin should have the formula $C_6H_4<\begin{matrix}O\\O\end{matrix}>C(OH)-CH_3$, and is the acid resorcin ether of ortho-acetic acid or metaphenyleneorthoacetate. This view is in accordance with the properties of the compound, whereas the formula given by the discoverers $C_6H_3\begin{matrix}(OH)_2\\CO.CH_3\end{matrix}$ — is in direct opposition to the compound yielding only a monoacetyl derivative, and its decomposition into resorcin and sodium acetate by boiling with aqueous sodium hydrate.

with an aqueous solution of sodium hydrate, sodium acetate and the yellow sodium derivative of salicylresorcin ether are formed. The analysis shows that salicylresorcin ether contains one hydroxyl group.

$$C_6H_4\begin{matrix}O\\CO\end{matrix}>C_6H_3OH + (C_2H_3O)_2O$$

$$= C_6H_4\begin{matrix}O\\CO\end{matrix}>C_6H_3OOCCH_3 + CH_3COOH.$$

0.2326 gram of substance, dried at 100°, gave 0.6063 gram of CO_2 and 0.0882 gram of H_2O.

	Theory for $C_{13}H_7O_3(C_7H_3O)$.	Found.
C	70.86	71.08
H	3.82	4.21

Action of Zinc Chloride on Salicylic Acid and Orcin.

A mixture of ten grams of orcin and 10 grams of salicylic acid was melted and 8 grams of powdered zinc chloride gradually added. The flux soon became yellow, and gradually changed to a dark brown color. After heating two hours, at a temperature sufficient to keep it in a melted state, the flux was poured into hot water, boiled out for several minutes and filtered. The dark residue was extracted several times with a solution of sodium carbonate, filtered, and the insoluble part crystallized three times from hot alcohol. The analysis gave the following numbers: 0.2136 gram of substance, dried at 100°, gave 0.5861 gram of CO_2 and 0.0900 gram of H_2O.

	Theory for $C_{14}H_{10}O_3$.	Found.
C	74.34	74.75
H	4.42	4.72

The substance crystallizes from hot alcohol as straw-colored, silky needles, melting at 140°. They are insoluble in cold and hot water; sparingly soluble in cold, more easily in hot alcohol. With alkalis they combine to form metallic derivatives, which are somewhat more soluble in water than the corresponding derivatives of salicylresorcin ether. Fluxed with caustic potash they are decomposed into salicylic acid and orcin. About three grams of the substance were obtained by using 10 grams orcin. It may be called salicylorcin ether or methyloxybenzophenone oxide.

$$C_6H_4\begin{matrix}OH\\COOH\end{matrix} + C_6H_3\begin{matrix}(OH)_2\\CH_3\end{matrix} = C_6H_4\begin{matrix}O\\CO\end{matrix}>C_6H_3\begin{matrix}OH\\CH_3\end{matrix} + H_2O.$$

Only the sodium derivatives of salicylorcin ether have been examined. A boiling alcoholic solution of the substance was poured into an excess of strong aqueous caustic soda. In a few moments long yellow needles separated from the solution. These were filtered, washed with alcohol and dried on the air. They contain water of crystallization, which is not completely given off until they are heated to 125°.

I. 0.5412 gram of substance, air-dried, heated to 125°, lost 0.0520 gram of H_2O.

II. 0.5345 gram of substance, air-dried, heated to 125°, lost 0.0495 gram of H_2O.

0.6870 gram of substance, dried at 125°, gave 0.2047 gram of Na_2SO_4.

	Theory for $C_{14}O_3H_9Na$.	Found. I.	II.
Na	9.28	9.63	
$1\frac{1}{2}H_2O$	9.45	9.60	9.24

A compound corresponding to the disodium salicylresorcin ether was not obtained. The analyses of the sodium derivative, obtained in a manner as already described for the resorcin compound, gave sodium percentages between those of the mono- and di-sodium compounds.

I. 0.6440 gram of substance, dried at 105°, gave 0.2555 gram of Na_2SO_4.

II. 0.6993 gram of substance, dried at 120°, gave 0.2813 gram of Na_2SO_4.

	Theory for $C_{14}O_3H_9Na,NaOH$.	Found. I.	II.
Na_2	15.93	12.85	13.03

Action of Acetic Anhydride on Salicylorcin-ether.

Equal parts of the orcin compound and fused sodium acetate were heated with four parts of acetic anhydride for three hours in a salt-water bath. The product of the reaction brought into cold water, solidified on standing to a white, crystalline mass, which was purified by three crystallizations from hot alcohol. The analysis gave the following numbers:

0.2300 gram of substance, dried at 100°, gave 0.6030 gram of CO_2 and 0.0930 gram of H_2O.

	Theory for $C_{14}H_9O_3(C_2H_3O)$.	Found.
C	71.64	71.50
H	5.47	4.49

From hot alcohol it is deposited on cooling as long white needles, resembling those of o-phthalic anhydride as obtained by sublimation. They are insoluble in hot water; easily soluble in hot, sparingly in cold alcohol. They melt at 151°-152°. Heated with an aqueous solution of caustic soda, the yellow sodium salicylresorcin ether and sodium acetate are formed.

Salicylresorcin ether and salicylorcin ether belong very probably to the same class of compounds as euxanthone and gentianin. With a view of obtaining these products the action of dehydrating agents on mixtures of oxysalicylic acid and resorcin, and methoxysalicylic acid and phlorglucin, will be next examined.

TUFTS COLLEGE, MASS., *April 4th*, 1883.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

BY W. A. NOYES.

It is well known that in many benzene derivatives, where a methyl group is protected from oxidation by chromic acid by the presence of a negative atom or group, the same methyl may be readily oxidized by potassium permanganate in alkaline solution. The question arises, Is this difference of action due to the fact that one oxidizing agent is acid while the other is alkaline, or is it due to the particular character of each agent? That some, at least, have thought the former to be true seems to be evident from the statement which Richard Meyer has recently given of Remsen's law: "Negative Atome oder Atomgruppen, welche sich in der Orthostellung gegen Kohlenwasserstoffreste im Benzolkern befinden, üben einen schützenden Einfluss auf diese Reste aus, wenn die Verbindungen mit sauren Oxydationsmitteln behandelt werden, Wirkt dagegen ein alkalisches Oxydationsmittel ein, so wird gerade umgekehrt der in Orthostellung befindliche Rest oxydirt."[1] The first paragraph in this statement of the law is almost exactly in Remsen's own words,[2] although the statement first given in this Journal[3] is more carefully worded and less general.

[1] Aromatische Verbindungen, p. 179.

[2] Remsen, Berichte der deutschen chemischen Gesellschaft, **11**, 2091.

[3] **1**, 36.

Up to the time when the experiments described in this paper were undertaken, the only acid oxidizing agents which had been studied in such a way as to yield results of value as bearing on the question here stated were chromic acid and nitric acid; and the alkaline agents were caustic potash and potassium permanganate. The action of chromic acid has been so fully discussed in this Journal that it requires only to be mentioned here. With this agent, very few exceptions to the protective action of ortho negative atoms or groups are known, and most of these occur where the group to be protected is large or unsaturated.

The action of nitric acid has been far less exhaustively studied than that of chromic acid. Enough, however, is known to show that no such general law holds for nitric acid as for chromic acid, since ortho-toluene derivatives may be oxidized to substituted benzoic acids by the former.[1] Yet, in the case of mesitylene and cymene-derivatives, methyl groups have, in a number of cases, been shown to be protected from oxidation with nitric acid by the presence of ortho negative atoms or groups.[2] But, when the negative atom or group is not present, only one of the hydrocarbon residues is oxidized by nitric acid, so that the negative atom seems rather to determine which group shall remain intact, than to exert a strong protective action.

Of the alkaline oxidizing agents, caustic potash has been used almost exclusively in oxidizing phenol derivatives. On the basis of Jacobsen's experiments, Remsen[3] has shown that in these compounds caustic potash oxidizes most readily the methyl group which is ortho to the hydroxyl group.

The only alkaline agent which has been used in oxidizing derivatives of the same nature as those which have been studied so extensively with reference to the action of chromic acid, is potassium permanganate. This readily oxidizes methyl which is ortho to a negative atom or group. The cases of ortho-toluene derivatives thus oxidized are so numerous and so well known as not to require enumeration here. As regards substitution products containing more than one oxidizable residue, one of the most interesting cases is that of sulpho-cymene. R. Meyer and A. Baur[4] have shown that this compound potassium permanganate oxidizes the

[1] Kekulé, Berichte der deutschen chemischen Gesellschaft, **7**, 1007; Zincke, *Ibid.* 1502.

[2] Fittig and Storer, Annalen der Chemie, **147**, 8; Kelbe, Berichte, etc., **15**, 41; Landolph, Berichte, etc., **5**, 268.

[3] Berichte der deutschen chemischen Gesellschaft, **11**, 2091. [4] *Ibid.* **13**, 1495.

methyl group which is ortho to the sulphonic group *first*, in marked contrast to nitric acid which oxidizes only the propyl group. Remsen, who has repeatedly made use of this agent in studying the trisubstitution products of benzene, states[1] that where two groups are to be oxidized, the oxidation is best effected in two stages, the meta or para group with reference to a negative atom or group being first oxidized with chromic acid and afterwards the ortho methyl being oxidized with potassium permanganate.

Using the terms ortho, meta and para with reference to the position of hydrocarbon residues toward a negative atom or group, our present knowledge is about as follows: chromic acid either does not oxidize ortho groups at all or oxidizes them in very small amount; nitric acid can oxidize ortho groups, but, where there is a choice, oxidizes meta or para groups by preference; caustic potash has been used only with one class of compounds, but there oxides ortho groups; potassium permanganate in alkaline solution oxidizes ortho, meta and para groups, but, where there is a choice, in some cases at least, it oxidizes ortho groups by preference.

On the whole, then, the general statement of the law as regards acid and alkaline oxidizing agents is justified so far as the agents most frequently used are concerned, although the law in many cases does not hold absolutely. The experiments here described were undertaken for the purpose of determining whether the general statement of the law would hold for another alkaline oxidizing agent. The agent chosen was potassium ferricyanide with caustic potash.

Oxidation of the Nitro-toluenes.

The first substance selected for study was ortho-nitro-toluene. The specimen used in the experiments was procured from Kahlbaum in Berlin. It boiled at 221°–229° (cor.) and, as will be seen later, contained some paro-nitro-toluene.

The proportions used in the oxidation were, 2 grams of potassium ferricyanide, 23 grams of caustic potash, and 200 grams of water. Some experiments were made with a more concentrated solution of the ferricyanide, but the proportions given above were found to work best. The calculated amounts in accordance with the reaction:

[1] This Journal, 2, 414.

$$C_6H_4\begin{matrix}CH_3\\NO_2\end{matrix} + 6K_3FeCy_6 + 7KOH = C_6H_4\begin{matrix}COOK\\NO_2\end{matrix} + 6K_4FeCy_6 + 5H_2O,$$

are, 50 grams of potassium ferricyanide, 9.93 grams of caustic potash and 3.47 grams of nitro-toluene.

There were some secondary reactions which led to the evolution of ammonia and the formation of considerable quantities of potassium carbonate and ferric oxide; but, as all of these were formed when the oxidizing mixture was boiled alone, the reactions leading to their formation were not especially studied.

The mixture, as described above, was boiled for two or three hours with an inverted condenser. At the end of this time the ferricyanide was mostly reduced to ferrocyanide, and there always remained some unoxidized nitro-toluene. The latter was distilled off with water-vapor. About two grams of nitro-toluene were recovered from eight grams oxidized in the proportions given above. After the nitro-toluene had been removed, the fluid was filtered from the ferric oxide which always separated, and the filtrate was acidified with hydrochloric acid and extracted with ether. In acidifying it was found best to add only enough acid to a little more than decompose all the carbonates present, since, if a large excess of acid was added, on shaking with ether a great mass of hydroferrocyanic acid was precipitated, which interfered very much with further work. Hydroferrocyanic acid was found to be stronger than any of the substituted benzoic acids worked with, and so there arose no difficulty from there being no free hydrochloric acid in the solution which was to be extracted.

On distilling off the ether a residue remained which proved to be a mixture of two acids. These were separated, partly by the different solubility of the acids in water, and partly by the different solubility of their barium salts.

One barium salt crystallized in thin yellow prisms which were difficultly soluble in cold water. The acid separated from these fused at 240° (cor.) The air-dry salt was analyzed with the following results:

I. 0.2486 gram of the salt lost 0.0396 gram H_2O at 150° and gave 0.1041 gram $BaSO_4$.

II. 0.2397 gram of the salt lost 0.0385 gram H_2O at 150° and gave 0.1015 gram $BaSO_4$.

	Calculated.		Found. I.	Found. II.
$(C_7H_4NO_4)_2$	332	59.39	...	...
Ba	137	24.51	24.62	24.90
$5H_2O$	90	16.10	15.93	16.06

This salt was accordingly that of para-nitro-benzoic acid. It evidently came from para-nitro-toluene which was mixed with the ortho compound.

For the sake of completeness in this part of the work, one gram of para-nitro-toluene (fusing point 53°) was oxidized by boiling for three hours with 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100 grams of water. The filtrate from the ferric oxide was evaporated to a small bulk and, when cold, filtered from the potassium ferrocyanide which crystallized out, and the para-nitro-benzoic acid in the filtrate precipitated with hydrochloric acid. The acid thus obtained fused at 240°–241° (cor.). The analysis of the barium salt gave the following results:

0.3437 gram of the salt lost 0.0552 gram H_2O at 140° and gave 0.1431 gram $BaSO_4$.

	Calculated.	Found.
Ba	24.51	24.48
$5H_2O$	16.10	16.06

The second acid obtained from the oxidation of the mixed nitro-toluene was far more soluble in water. Its barium salt was also very soluble, even in cold water. From a concentrated solution the salt separated in concentrically grouped crystals of an orange yellow color. The acid separated from a portion of these fused at 146° (cor.). Claus and Mallmann[1] gave 146.5° as the fusing point of ortho-nitro-benzoic acid. The free acid had a sweet taste, and dissolved in caustic potash or soda with an intense yellow color. The analysis of the barium salt gave the following results:

I. 0.2366 gram of the salt lost 0.0253 gram H_2O at 160° and gave 0.1050 gram $BaSO_4$.

II. 0.2162 gram of the salt lost 0.0230 gram H_2O at 160° and gave 0.0968 gram $BaSO_4$.

III. 0.1992 gram of the salt lost 0.0210 gram H_2O at 150°. The barium determination was lost.

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 760.

	Calculated.		Found. I.	II.	III.
$(C_7H_7NO_4)_2$	332	63.47	...	...	...
Ba	137	26.20	26.30	26.32	...
$3H_2O$	54	10.33	10.69	10.64	10.54

The salt used in analysis III was recrystallized from water.

A rough estimate was made of the yield from the oxidation. From 8 grams of nitro-toluene oxidized as described above, two grams of unoxidized nitro-toluene were recovered, and barium salts were obtained corresponding to about 1.2 gram of para-nitro-benzoic acid and 1.7 gram of the ortho acid. No great exactness is claimed for these numbers.

Thus the proof was complete that both ortho and para-nitro-toluene are oxidized to the corresponding nitro-benzoic acids by potassium ferricyanide and caustic potash.

It was thought that something might be learned about the relative ease with which the para and ortho compounds are oxidized by oxidizing the portion of nitro-toluene which had been left unacted upon by the mixture. If this should leave only ortho-nitro-benzoic acid, it would indicate that the para compound was most easily acted upon and had been entirely oxidized, leaving only ortho-nitro-toluene. The oxidation was conducted as before and again a mixture of two acids was obtained, one fusing at 139°–140°, and the other at 239°. The amount obtained was not enough for complete purification and analysis, but there can be no doubt that both ortho- and para-nitro-benzoic acids were formed. Hence there is no indication whether ortho- or para-nitro-toluene is oxidized more easily. Both compounds are oxidized in the same manner as by potassium permanganate in alkaline solution.

Oxidation of the Brom-toluenes.

Only an outline of the work done with ortho-brom-toluene will be given here, as, in spite of much time which has been spent on the subject, no decisive result has yet been obtained. The methods in which the attempt has been made to determine whether ortho-brom-toluene is oxidized by the mixture I am studying are as follows: (1) Oxidation of liquid brom-toluene, from Kahlbaum; this contained three per cent. of benzyl bromide (determined by the

method described by Jackson[1]), and gave about 1.6 per cent. of the amount of brom-toluene used, in benzoic acid, and a small amount of para-brom-benzoic acid. A careful examination of the barium salts of the acids obtained, based on the solubility of ortho-brom-benzoate of barium in alcohol, failed to show any ortho-brom-benzoic acid. A trace may, however, have been present. (2) Oxidation of brom-toluene nearly freed from benzyl bromide by heating with alcoholic ammonia; this gave chiefly para-brom-benzoic acid and a trace of benzoic acid, but no evidence of ortho-brom-benzoic acid. (3) Oxidation of brom-toluene partly purified from the para compound by boiling for twenty-four hours with an excess of the chromic acid oxidizing mixture; this gave a small amount of an acid fusing above 230°. (4) Oxidation of a brom-toluene boiled for fifty hours with a large excess of the chromic acid mixture; one gram of this brom-toluene, when treated with 25 grams of ferricyanide, gave between 3 and 4 milligrams of an acid for which no satisfactory fusing point could be obtained. By oxidizing a very small portion of the same brom-toluene with potassium permanganate, acids were easily obtained fusing at 246°–248° and at 141°–143°. One gram of *para*-brom-toluene oxidized with 25 grams of the ferricyanide in exactly the same way that was followed with the brom-toluene last mentioned gave 6.4 milligrams of para-brom-benzoic acid.

Different specimens of para-brom-benzoic acid mentioned above fused at 248° to 255°; the purest at 252°–253° (cor.), exactly the same point which was found for a specimen of the pure acid obtained by oxidizing para-brom-toluene with the chromic acid mixture. The benzoic acid fused at 120°, and its character was also established by an analysis of the barium salt.

0.0503 of the salt lost 0.0049 gram H_2O at 130° and gave 0.0305 gram $BaSO_4$.

	Calculated for $(C_6H_5CO_2)_2Ba + 2H_2O$.	Found.
Ba	33.01	33.02
$2H_2O$	8.67	9.02

While these experiments have not yet established whether ortho-brom-toluene is oxidized at all by potassium ferricyanide, and I intend to return to this point as soon as proper material can be obtained, they do show that, if there is any oxidation, it takes

[1] This Journal, **2**, 4.

place with very great difficulty. The only other possible explanation of the results obtained would seem to be that ortho-brom-benzoic acid is unstable towards this oxidizing agent and is destroyed as fast as it is formed. This explanation was considered very improbable, but it was made the subject of a special experiment. 0.0055 gram of ortho-brom-benzoic acid was boiled for three hours with 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100 cc. of water. The filtrate from the ferric oxide was evaporated somewhat, the potassium ferrocyanide, which crystallized out on cooling, was filtered off, the filtrate acidified with sulphuric acid and extracted with ether. The residue left on distilling off the ether was dissolved in a little ether and the solution evaporated on a watch-glass. It left 0.0048 gram of the acid. This fused, without further purification, at 132°–133°. It was white and dry.

It was very noticeable in this experiment that the reduction of the ferricyanide was even more complete than usual, although the boiling was continued no longer than in other experiments, and all oxidation must have been practically confined to action of the ferricyanide on itself. This furnishes a partial explanation of the very small amount of para-brom-toluene which can be oxidized with a given amount of potassium ferricyanide. Evidently the para-brom-toluene is oxidized with greater difficulty than the ferricyanide itself, and hence the oxidizing action is directed chiefly toward the latter until the reduction of the ferricyanide is complete. There is, as it were, a balance struck between the amount of the brom-toluene and the ferricyanide which is oxidized. Of course, the amount of the former cannot be increased by lengthening the time of boiling.

The amount of the para-brom-toluene which can be oxidized by this method is so small that it was difficult to obtain enough of the para-brom-benzoic acid for an analysis. A small amount of the barium salt was prepared from the acid obtained by several oxidations. It was difficultly soluble in water and crystallized in small white leaflets, appearing exactly like the salt prepared from the acid obtained in the usual manner. The analysis was performed with the utmost care on a balance giving constant weights to $\frac{1}{10}$ milligram.

0.0145 of the salt lost no water at 120° and gave 0.0064 gram $BaSO_4$.

	Calculated for $(C_6H_4BrCO_2)_2Ba$.	Found.
Ba	25.5	25.9

All the properties of the acid and salt, so far as studied, agreed exactly with those of the acid and salt prepared in the usual manner. The acid fused at 252°–253° (cor.).

For the purpose of comparison, one gram of toluene (Merck's; boiled 110°–112°) was oxidized with 25 grams of potassium ferricyanide in the same manner as described above. About nine milligrams of benzoic acid were obtained. It fused at 120°.

A summary of the results thus far obtained is as follows:

I. Ortho-nitro and para-nitro-toluene are oxidized to the corresponding nitro-benzoic acids by potassium ferricyanide and caustic potash, as they are by potassium permanganate in alkaline solution and by nitric acid. The oxidation takes place quite readily.

II. Toluene and para-brom-toluene are oxidized by potassium ferricyanide with great difficulty, and the latter with greater difficulty than the former. Ortho-brom-toluene is oxidized, if at all, with very great difficulty.

The effect of the nitro-group upon the toluene molecule deserves a word. It is an effect for which there are some analogies among the other nitro derivatives of benzene, but which, I think, has not been noticed in any case exactly like this before. More than twenty-five times as much of para-nitro-toluene as of toluene itself is oxidized by 25 grams of potassium ferricyanide. This is a good illustration of the fact so often stated, that an atom or group affects all parts of a molecule in which it is situated, no matter how far from it those parts may be.

I cannot conclude without expressing my hearty thanks to Professor Remsen for valuable suggestions given me with reference to this work before it was undertaken, and for the kindness with which he furnished me with some of the materials necessary for these experiments.

UNIVERSITY OF MINNESOTA, *March* 27, 1883.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XIV.—EXPERIMENTS WITH DERIVATIVES OF NAPHTHALENE.

By Ira Remsen.

The facts which have been established by earlier investigations of this series led to the belief that the oxidation of the α- and β-sulphamides of naphthalene with potassium permanganate would yield results of value in connection with some of the interesting questions involved in the isomerism of the substitution products of naphthalene and of phthalic acid. There were three points which it was desired particularly to accomplish in this investigation: (1) to establish, if possible, a direct line of connection between the sulphonic acids of naphthalene and the oxyphthalic acids; (2) to determine the influence of the presence of alkali on the oxidation phenomena; and (3) to determine whether either or both the sulphamine-phthalic acids can yield anhydrides corresponding to the sulphinides described in earlier papers. The part of the investigation, an account of which is here given, has to deal with the best conditions for passing from the sulphamides of naphthalene to the corresponding derivatives of phthalic acid. The more detailed study of these derivatives is now in progress, Mr. E. H. Keiser having undertaken the study of the β-compounds and their transformations, while Mr. H. N. Stokes is engaged in a similar study of the α-derivatives.

Oxidation of α- and β- Naphthalenesulphamides.

By W. J. Comstock.

The lead salts of α- and β-naphthalenesulphonic acids were made and separated according to the directions given by Merz[1] and by Merz and Weith.[2] To make the sulphamides the lead salts were treated directly with phosphorus pentachloride and ammonia. The results were as satisfactory as those obtained by Maikopar,[3] who used the potassium salts. After the action of the ammonia was over, the cooled mixture was poured upon the filter and washed with cold water. The amides were separated from

[1] Zeitschrift für Chemie, 1868, 393.
[2] Berichte der deutschen chemischen Gesellschaft, **3**, 196.
[3] Zeitschrift für Chemie, 1869, 711.

inorganic matter by dissolving in strong alcohol and recrystallising from water. Thus both amides were easily obtained in pure condition with the properties ascribed to them by previous writers.

Preliminary experiments with nitric acid as the oxidising agent gave unsatisfactory results, and it was only after we had experienced repeated failures that we finally succeeded with potassium permanganate.

Experiments in the α-series.

Experiment 1.—10 grams of the α-amide were oxidised in neutral solution with 48 grams potassium permanganate in one litre of water. The mixture was kept in the water-bath at 100° until the permanganate was completely reduced. This took place in two hours. After separating the oxides of manganese the solution was evaporated to about 250 cc., acidified with hydrochloric acid and extracted with ether. The extract weighed 3.5 grams, and on recrystallisation from water proved to be pure phthalic acid.

The solution after extraction with ether was evaporated to dryness and extracted with alcohol. The compound extracted was *α-sulphophthalic acid*, as was shown by the formation of the neutral barium salt. The free acid was not obtained pure enough nor in sufficient quantity for examination. It is very soluble in water, and somewhat less soluble in alcohol. It cannot be extracted from aqueous solutions by ether.

Neutral barium α-sulphophthalate, $\left(C_6H_3\left\{\begin{matrix}SO_3O\\COO\\COO\end{matrix}\right.\right)_2Ba_3 + 8H_2O$. This salt was made by boiling a dilute solution of the acid for some time with an excess of barium carbonate. It is difficultly soluble in boiling water and crystallises on cooling. The crystals appear under a lens to be aggregations of needles, but under the microscope these are seen to be aggregations of small plates, clear and transparent. The air-dried salt lost seven molecules of water below 150°, but retained the other molecule at a much higher temperature.

.277 gram lost at 150° .0342 gram H_2O; at 250° it lost .0039 gram more of H_2O.

	Calculated.	Found.
$8H_2O$	13.83	13.76

.2389 gram anhydrous salt gave .1861 gram $BaSO_4$.

Anhydrous salt.	Calculated.	Found.
Ba	45.82	45.80

The salt is very soluble in dilute hydrochloric acid, and does not yield an acid salt by long standing of the concentrated solution.

Secondary lead salt, $C_6H_3\begin{cases}SO_3O\\COO\\COOH\end{cases}\!\!>Pb + 1\tfrac{1}{2}H_2O$. This was prepared by boiling a dilute aqueous solution of the acid with lead carbonate for some time, and filtering while hot from the excess of lead. When the solution cools the salt settles in flocculent form, and afterwards changes slowly into small prismatic crystals. This change takes place more quickly when the flocculent precipitate is collected on the filter and kept in moist condition under a bell-jar for several days. Some of the salt treated in this way and then dried in the air appeared to be entirely changed into the prismatic crystals.

.2644 gram of this air-dried salt lost .0148 gram H_2O at 150° and gave .1701 gram $PbSO_4$.

	Calculated.	Found.
Pb	43.31	43.95
$1\tfrac{1}{2}H_2O$	5.65	5.60

Experiment 2.—10 grams *a*-amide were dissolved in 500 cc. of water, with addition of 8 grams potassium hydroxide, and to this were added 48 grams potassium permanganate dissolved in one litre of water. The reduction of the permanganate was complete in about 36 hours at 100°. The solution was treated as in Experiment 1. Some phthalic acid separated out after acidifying, and more was extracted by ether. After evaporating the solution to dryness and extracting with alcohol, a small quantity of the *a*-sulphophthalic acid was obtained and recognised by means of its neutral barium salt. No sulphaminephthalic acid could be detected.

Experiment 3.—Two portions of nine grams of the *a*-amide, each dissolved in 450 cc. of water, with 7 grams potassium hydroxide, were treated each with 40 grams potassium permanganate dissolved in 900 cc. of water. The reduction of the permanganate was complete in each case in about twelve hours at 100°. After filtering from the oxides of manganese the portions were united, concentrated to about 350 cc. and acidified with hydrochloric acid. On cooling there separated about five grams of needle crystals about one centimeter long. Upon recrystallisation from water the

crystals were much shorter and thicker. These crystals proved to be *mono-potassium α-anhydrosulphaminephthalate*, $C_6H_3\left\{\begin{matrix}SO_2\\CO\\COOK\end{matrix}\right\}NH + H_2O$. The salt can be easily crystallised from hot water or alcohol. It is insoluble in ether. It was shown to contain both nitrogen and sulphur, and gave off ammonia when fused with potassium hydroxide.

.3126 gram of the air-dried salt lost .0200 gram H_2O at 160° and gave .0950 gram K_2SO_4.

.3969 gram lost .0258 gram H_2O at 160°, and after fusing with KOH and KNO_3 gave .3225 gram $BaSO_4$.

	Calculated.	Found.	
S	11.30	11.16	
K	13.81	13.64	
H_2O	6.36	6.40	6.50

Whether the water which is given off at 160° is water of crystallisation or water of constitution it is impossible to decide. It is certain, however, that after the salt has been heated to 160° an anhydride is left, and it is difficult to see what this can be but a new example of the class of bodies known as sulphinides which have been studied in this laboratory.

Mono-silver α-sulphaminephthalate, $C_6H_3\left\{\begin{matrix}SO_2NH_2\\COOH\\COOAg\end{matrix}\right.$. This was obtained by adding silver nitrate to the aqueous solution of the above-described potassium salt. The same salt is formed when the silver nitrate solution is acidified with nitric acid. It can be easily crystallised from its hot solutions in water or dilute nitric acid. It crystallises in colorless transparent needles. The air-dried needles did not lose in weight at 180°, and when heated much above that temperature became dark-colored, apparently owing to decomposition.

.2955 gram gave .0903 gram metallic silver.

	Calculated.	Found.
Ag	30.68	30.56

In this case the formation of an anhydride, observed in all similar cases, does not seem to take place.

In the above experiments, the only one in which the sulphamine acid was obtained was that in which the oxidation was made in alkaline solution and without excess of the oxidising agent. In this case also there was found but a small quantity of phthalic acid. It is, of course, possible that the sulphamine acid was formed in the other cases, and the amido group split off by the hydrochloric acid when the solution was evaporated to dryness. At any rate, the proportion of the α-sulphaminephthalic acid formed in the third experiment was much larger than in the others.

Experiments in the β-series.

Experiment 1.—10 grams of the β-amide were dissolved in one litre of water with 7 grams potassium hydroxide, and to this was added one litre of water containing 48 grams potassium permanganate. The permanganate was reduced in about thirty hours at 100°. After separating the oxides of manganese and concentrating to about 250 cc. the solution was acidified with hydrochloric acid. It deposited on cooling about three grams of small prismatic crystals. After recrystallising once from water these crystals contained sulphur, but no nitrogen, and proved to be *di-potassium β-sulphophthalate*, $C_6H_3\begin{cases}SO_3OK\\COOK\\COOH\end{cases} + 2H_2O$. The salt is very easily soluble in water and almost insoluble in both cold and hot alcohol.

.3207 gram of the air-dried salt lost .0314 gram H_2O at 150° and gave .1572 gram K_2SO_4.

	Calculated.	Found.
K	21.83	22.00
$2H_2O$	10.05	9.79

The salt has a strongly acid reaction, and its aqueous solution dissolved potassium carbonate with effervescence, but no crystallised neutral salt could be obtained from the very strong solution.

A very small quantity of phthalic acid was obtained from the solution by extraction with ether after the separation of the acid potassium sulphophthalate; and although the residue after evaporating the solution still contained some organic matter, this could not be separated by extracting with hot or cold alcohol.

Experiment 2.—24 grams of the β-amide were dissolved in two litres of water with 16 grams potassium hydroxide, and oxidised with 108 grams potassium permanganate dissolved in two litres of

water. The oxidation was made in two equal portions, and in each portion the permanganate was reduced in about twelve hours. After treating in exactly the same manner as in the experiment preceding, the crystals obtained were entirely different in appearance, and proved to be *mono-potassium β-sulphaminephthalate*, $C_6H_3\begin{cases}SO_2NH_2\\COOH\\COOK\end{cases} + 2\frac{1}{2}H_2O$. The salt crystallises in silky needles, having sometimes a length of half a centimeter and collected in groups radiating from a centre. It had a light straw color after three recrystallisations. It is easily soluble in water with a strongly acid reaction, and when fused with potassium hydroxide gives off ammonia.

.2800 gram of the air-dried salt lost .0401 gram H_2O at 180° and gave .0754 gram K_2SO_4.

	Calculated.	Found.
K	11.92	12.09
$2\frac{1}{2}H_2O$	13.72	14.32

But a small quantity of phthalic acid was found in this case, so that there must still have been a considerable quantity of the sulphaminephthalate in the solution, which was shown to contain organic matter.

In the β-series as in the α-series the most favorable condition for obtaining the sulphamine acid seems to be maintained when no excess of permanganate is present beyond the quantity required theoretically to convert the amide into the corresponding substituted phthalic acid.

It is impossible to state certainly from this work which of the sulphophthalic acids Loew obtained[1] by heating phthalic acid with sulphuric anhydride. But from the conduct of the lead salt of his acid, which he states was decomposed with separation of lead sulphate by gently warming the aqueous solution, it could not have been the α-acid obtained by me, for the lead salt of this acid was boiled for several hours without decomposition.

The mono-potassium β-sulphaminephthalate is probably the same salt as that obtained by Jacobsen[2] by oxidising sulphamine-orthotoluic acid, although he has not described his salt in sufficient detail to make the identity certain.

[1] Annalen der Chemie, **143**, 257.

[2] Berichte der deutschen chemischen Gesellschaft, **14**, 42.

ON THE PREPARATION AND REACTIONS OF CROTONALDEHYDE.

By Spencer B. Newbury.

Two years ago I published in the *Comptes rendus* (Paris, Jan. 24th, 1881), the description of a method for the preparation of crotonaldehyde, founded upon Wurtz's discovery that aldol, $CH_3CHOH\ CH_2CHO$, is completely resolved into water and crotonaldehyde. This method, which subsequent experiments have led me to modify somewhat, is briefly as follows:

One volume of aldehyde (or paraldehyde) is mixed with one volume of water and two volumes of concentrated hydrochloric acid, and the whole allowed to stand for some days at the ordinary temperature of the laboratory. In case aldehyde is employed the solution must be kept cold during the addition of the acid; with paraldehyde no such precaution is necessary. On standing, the mixture assumes a brown color, and becomes finally quite dark and opaque. The progress of the condensation may be tested from time to time by neutralizing a small portion of the solution with sodium carbonate. The right point has been reached when the neutralization causes the separation of a thick oily layer, which becomes indistinctly crystalline after standing some hours. The whole is then neutralized, the layer of higher products of condensation removed by skimming or filtration, and the solution exhausted by shaking repeatedly with ether. On distilling off the ether, aldol, mixed with paraldehyde and some higher products (dialdan, &c.) remains in the retort. By distillation under reduced pressure the aldol may be obtained nearly pure, as a thick, syrupy, colorless liquid. The fraction which passes over between 90° and 110° under a pressure reduced to 2 cm. of mercury is sufficiently pure for the preparation of crotonaldehyde.

The yield of aldol seems to be somewhat greater if less acid be employed, but the reaction proceeds much more slowly. Under favorable circumstances I have obtained 450–500 grams of aldol from 2 kg. of paraldehyde. The yield of crotonaldehyde is about 50 per cent. of the aldol employed, hence from 10 to 12 per cent. of the aldehyde used.

Aldol boils, with more or less complete decomposition into water and crotonaldehyde, at about 185°. This decomposition begins at about 140°, and by keeping the substance at this temperature in an oil-bath, and allowing the products of decomposition to distill over, the maximum yield of crotonaldehyde may be obtained. The product is then freed from water by means of calcium chloride or potassium carbonate, and rectified. Pure, dry crotonaldehyde boils at 105°.

The derivatives of crotonaldehyde have been but little studied, chiefly for the reason that they are for the most part very unstable. Kekulé[1] obtained the compound "crotonylene chloride," or rather dichloropseudobutylene, $CH_3-CH=CH-CHCl_2$, by the action of phosphorus pentachloride on crotonaldehyde. He describes in the above paper his repeated attempts to remove the two atoms of chlorine from the above compound by boiling with alcoholic potash, by which he hoped to obtain diethylene, according to the reaction:

$$\begin{matrix} CH_3-CH & & CH-CH \\ \| & = 2HCl + & \| \quad \| \\ Cl_2CH-CH & & CH-CH \end{matrix}$$

In this he was unsuccessful, for after boiling for many hours the substance was not materially affected. In my own experiments I found the dichloro compound to be equally indifferent to the action of an alcoholic solution of sodium ethylate, while my endeavor to derive a chlor-acetal from crotonaldehyde by passing gaseous HCl through an alcoholic solution of the latter was also unsuccessful; the solution became dark brown in color, and the resulting product decomposed completely on heating.

By the action of bromine on the dichloropseudobutylene described by Kekulé, I obtained a heavy, oily liquid, the analysis of which agrees closely with that required by the formula $CH_3CHBrCHBrCHCl_2$, or dichloropseudobutylene dibromide. This compound is at once decomposed on heating above 100°, and hence cannot be distilled. On boiling with a dilute solution of potassium carbonate, carbon dioxide was evolved, but after several days' boiling the resulting product still showed the presence of both Cl and Br. One fraction, boiling at 115°-120°, showed approximately the composition C_4H_6BrClO.

[1] Liebig's Annalen, **162**, 99.

Crotonaldehyde combines readily with bromine, forming a heavy, oily liquid, the vapor of which attacks the mucous membrane of the nose and eyes most painfully. This compound shows the composition $CH_3CHBrCHBrCHO$. It decomposes at once on heating, and all my attempts to replace the bromine atoms by hydroxyl groups were unsuccessful.

CORNELL UNIVERSITY, *April*, 1883.

ELECTROLYSIS OF BISMUTH SOLUTIONS.

BY N. WILEY THOMAS AND EDGAR F. SMITH.

In estimating bismuth in the electrolytic way, solutions of the sulphate, alkaline solutions of the citrate, and the latter in presence of free citric acid were used.

I. A weighed quantity of bismuthous oxide was dissolved in about 1 cc. conc. sulphuric acid and then diluted to 100 cc. with distilled water. 10 cc. of this solution contained .0358 gram metallic bismuth. In two experiments with this solution 10 cc. of the same were placed in a small platinum crucible surrounded by a stout copper wire leading from the zinc pole of a three (one quart) celled bichromate battery. Into the solution dipped a platinum wire connected with the carbon pole. The current ran three hours, was then interrupted and the liquid quickly removed from the vessel. The deposited metallic bismuth, compact and perfectly regular, was washed first with water, then with alcohol, after which it was dried and weighed.

Found, *a*, .0354 gram Bi; *b*, .0358. Required, .0358 gram Bi.

In two additional experiments, instead of placing the bismuth solution in a crucible it was put into a beaker glass, diluted up to 100 cc. with water, and a platinum crucible connected with the zinc pole was suspended in the liquid. The platinum wire from the carbon pole extended down below the crucible. The solution being so much more dilute than in *a* and *b*, the current was allowed to run five hours before being interrupted. The crucible, upon the outside of which the metal had deposited in a homogeneous

form, was then removed, the coating washed as before, dried and weighed.

Found, *c*, .0310 gram Bi; *d*, .0355. Required, .0358.

The liquid remaining from *c* gave a brownish coloration with hydrogen sulphide.

This method can be employed with satisfactory results by using moderately concentrated solutions and having the wire from the carbon pole not too far removed from the vessel upon which the metal is to be deposited.

II. Bismuth hydrate was dissolved in conc. citric acid and the liquid then made alkaline with sodium hydrate. The quantity of metal in solution was determined and definite portions of the liquid then electrolysed.

Found, 1, .0356; 2, .0358; 3, .0358. Required, .0356.

The slight difference is probably due to the difficulty experienced in removing the alkali and to errors in weighing. Only two of the previously mentioned cells were used. The time allowed for the precipitation was three hours. The deposit in each case was compact and regular.

III. An alkaline citrate solution of bismuth was acidified with citric acid and definite portions of it subjected to the action of the current. Two cells were employed and the average time for precipitation was two and a half hours. Required Bi = .0356 gram; found:

1.—.0358	7.—.0357
2.—.0353	8.—.0356
3.—.0352	9.—.0357
4.—.0358	10.—.0358
5.—.0356	11.—.0358
6.—.0358	12.—.0356

Heat does not hasten the precipitation. In some instances when the current was not very brisk a slight deposition of oxide upon the wire was observed, but this invariably disappeared before the action of the current was interrupted.

MUHLENBERG COLLEGE, ALLENTOWN, PA., *February* 9, 1883.

ON SOME PROPERTIES OF PHENYLSULPHONACETIC ETHERS.

By A. Michael and A. M. Comey.

The important investigations of Geuther, Wislicenus, V. Meyer, and others, on ethyl acetyl acetate and nitroalkanes have shown that in organic compounds the properties of the hydrogen of a hydrocarbon group are dependent on the nature of the groups joined to the same carbon. While in ethyl acetate the acid action of the group $COOC_2H_5$ does not suffice to render a hydrogen of the methyl group sufficiently negative to be replaceable by metals, this property is shown when the combined action of the acetyl and $COOC_2H_5$ groups, or two of the latter, exert their influence on a methylene group. We have considered as worthy of investigation the question, whether in organic compounds the replaceability of hydrogen by metals only occurs under the combined influence of two organic negative radicals; or if these radicals may be wholly or partially replaced by radicals of inorganic acids without loss of this property. The present note will show that the acetyl group of ethyl acetyl acetate when replaced by the acid radical $C_6H_5SO_2$, the sulphonether still has the property of forming metallic derivatives. We hope in the course of our investigation to examine the behavior of the following compounds towards sodium or sodium ethyloxide, $CH_2(SO_2OC_2H_5)_2$, $CH_3\overset{SO_2OC_2H_5}{\underset{COOC_2H_5}{}}$, $CHCl_2COOC_2H_5$,[1] $CH(OC_2H_5)_2COOC_2H_5$ and $CH_3SO_2OC_2H_5$.

The phenylsulphonacetic ether used in our experiments was prepared by the action of ethyl chloracetate on sodium phenylsulphinate.[2] To an alcoholic solution of the sulphinate, obtained by adding the equivalent amount of ethylsodiumoxide to a solution of

[1] It is not impossible that the difference of the behavior of some organic haloids towards H_2O and caustic alkalis may be due to the action of the halogen on the hydrogen. Thus, to take an example, the first phase of the action of KOH on ethylene bromide may be the formation of a certain amount, dependent on the law of mass and affinity, of the compound $CHKBr-CH_2Br$, which immediately splits into $CHBr-CH_2$ and KBr. A series of reformations and decompositions of $CHKBr-CH_2Br$ would then take place until all is decomposed. That this cannot happen in the action of water on ethylene bromide is evident. I am well aware that this view is open to serious objections, but believe it to be worthy of consideration.—A. M.

[2] That sulphones are obtained in this manner was first shown by P. Claesson (J. pr. Chem. [2], **15**, 223). R. Otto (Ber. 1880, 1272), and later, S. Gabriel (*ibid.* 1881, 883), have apparently overlooked that research.

the acid in absolute alcohol, the molecular weight of ethyl chloracetate was added and the mixture heated for four or five hours in a hot water-bath. The sodium sulphinate dissolved on heating, and a deposition of sodium chloride was soon noticed. After the reaction was over the alcohol was distilled off and the contents of the flask shaken out with water. The insoluble oil cannot be purified by distillation, as it undergoes decomposition below its boiling point. If it is allowed to stand for several hours, large crystals separate out of the oil, which may be removed; or the oil allowed to stand for several days, when it solidifies almost completely. The yield obtained was about 80 per cent. of the amount indicated by the theory. The substance was purified by crystallisation from absolute alcohol. A sulphur estimation, made by the method of Carius, gave the following result:

0.2292 gram of substance dried *in vacuo* gave 0.2360 gram of $BaSO_4$.

	Theory for $C_6H_5SO_2CH_2COOC_2H_5$.	Found.
S	14.04	14.14

Ethyl phenylsulphonacetate crystallises from alcohol in clusters of long prisms. It is insoluble in hot water, soluble in hot, but slightly in cold alcohol. The substance melts at 45°. Boiled with alkalis, the corresponding salt is formed, which, treated with acids, yielded phenylsulphonacetic acid.

The behavior of the ether towards sodium was first examined, but without obtaining very satisfactory results. On a solution of the ether in benzene no action was noticed in the cold; when the solution was heating to boiling, the sodium acted but very slowly, forming a white amorphous substance. Better results are obtained by mixing solutions of the ether and ethylsodiumoxide, in proportions of equal molecules in absolute alcohol; a method, as Conrad and Limpach[1] have shown, which gives the sodium derivative of ethyl acetyl acetate. A mixture of equivalent amounts of the two substances dissolved in absolute alcohol soon solidifies to a mass of voluminous white needles. They were filtered, washed well with absolute alcohol and dried *in vacuo*. A sodium estimation gave the following result:

0.6935 gram of substance gave 0.1955 gram of Na_2SO_4.

	Theory for $C_6H_5SO_2CHNaCOOC_2H_5$.	Found.
Na	9.30	9.13

[1] Annalen der Chemie, **192**, 153.

Ethyl sodiumphenylsulphonacetate is sparingly soluble in cold, moderately in hot alcohol. In water it is very soluble; the aqueous solution acidified gives a precipitate of the original ether, melting at 45°. An alcoholic solution of the compound when boiled gradually solidifies to a gelatinous mass, which is also obtained when hot solutions of the alcoholate and ether are mixed. This sodium product when heated gives a sublimate melting at 85°; when treated with acids, a product which is not the original ether. It will be further examined.

In the present note we shall confine ourselves to the proof that the sodium in the above compound can be replaced by monad hydrocarbon radicals, and reserve for a second paper to show that in the proper uses of the above class of compounds valuable methods for the syntheses of organic compounds have been found.

To an alcoholic solution of ten grams ethyl phenylsulphonacetate a solution of one gram sodium in absolute alcohol and five grams benzyl chloride were added. The precipitate of the sodium derivative dissolved on heating in a water-bath, and in a short time the formation of sodium chloride began. After heating for several hours the condenser was inverted and the alcohol evaporated. The oil remaining in the flask was poured in water; it gradually hardened to a crystalline mass. The substance was purified by crystallisation from absolute alcohol. On analysis it gave the following numbers:

I. 0.2300 gram of substance, dried *in vacuo*, gave 0.5362 gram CO_2 and 0.1228 gram of H_2O.

II. 0.2138 gram gave (Carius's method) 0.1442 gram $BaSO_4$.

	Theory for $C_{17}H_{18}O_4S$.	Found.
C	64.14	63.59
H	5.66	5.93
S	10.06	9.26

The formation of the substance may be represented as follows:

$$C_6H_5CH_2Cl + C_6H_5SO_2CH_2NaCOOC_2H_5 = \begin{matrix} C_6H_5CH_2 \\ C_6H_5SO_2 \end{matrix} CHCOC_2H_5 + NaCl.$$

Ethyl benzylphenylsulphonacetate is insoluble in cold and hot water; sparingly in cold, readily in hot alcohol. From alcohol it is obtained as short white prisms, melting at 95–96°. Treated

with an alcoholic solution of sodiumethyloxide it yields a sodium derivative, which is more soluble than the corresponding phenylsulphonether derivative. When heated with benzyl chloride the sodium compounds give the dibenzyl derivative, melting at 118°.

The mono-benzylether saponifies with difficulty. Heated with aqueous sodium hydrate, the decomposition of several grams was incomplete, even after boiling for eight hours. The saponification is easily effected by heating the substance with an excess of alcoholic caustic soda for several hours in a closed tube at 100°. The crystalline salt, which gradually separated from the solution on heating, was dissolved in water and the acid liberated by addition of a mineral acid. The examination of the substance showed that it contained no sulphur, and that it possesses all the properties of cinnamic acid. An analysis proved the identity beyond a doubt.

0.1982 gram of substance gave 0.5282 gram of CO_2 and 0.1010 gram of H_2O.

	Theory for $C_6H_5CHCHCOOH$.	Found.
C	72.97	72.69
H	5.40	5.64

The formation of cinnamic acid may be represented as follows:

$$C_6H_5CH_2CH(SO_3C_6H_5)COOC_2H_5 + 2KOH = C_6H_5CHCHCOOH + C_6H_5SO_3K + C_2H_5OH + H_2O.$$

This decomposition seems to be characteristic for this class of compounds. According to Valet[1] phenylsulphopropionic acid, $C_6H_5C_2H_3SO_3OHCOOH$, heated with caustic potash, decomposes easily in the potassium salts of cinnamic and sulphurous acids, a reaction which is perfectly analogous to the above described.

The proof that one of the hydrogens of the methylene group of ethyl phenylsulphonacetate may be replaced by sodium, renders it extremely probable that such compounds as $CH_2(SO_3OC_2H_5)_2$, $CH_2(SO_3C_6H_5)_2$ and $CH_2\begin{matrix}COOC_2H_5\\SO_3OC_2H_5\end{matrix}$ are likewise endowed with this property.

TUFTS COLLEGE, MASS., *April* 29, 1883.

[1] Annalen, **154**, 70.

REVIEWS AND REPORTS.

Analytical Chemistry.

Sulphur.—In order to determine the total amount of sulphur in illuminating gas, Theodore Poleck[1] recommends aspirating the products of combustion from an ordinary Bunsen burner, through an inverted funnel leading to a dilute solution of caustic soda to which bromine has been added. The sulphur dioxide is oxidized to sulphuric acid by this means, and may be determined as barium sulphate. The apparatus is inexpensive as compared with the usual forms used for this purpose, and it has been used by the author with satisfactory results since 1875.

A new method for determining Sulphur in Organic Bodies.—In the endeavor to furnish a method for determining sulphur in organic substances which shall be free from the objections to the methods of Liebig, Fahlberg and Iles, Weidel and Schmidt, and others, Peter Claësson[2] proposes the complete oxidation of the substance in a current of oxygen and nitric oxide, *i. e.* nitrogen tetroxide gas. A combustion tube somewhat longer than the furnace, is drawn out at one end and bent at a right angle. Next to the bend a roll of platinum gauze 7 centimetres long is placed; 10 centimetres from this is a boat containing fuming nitric acid; about 10 centimetres farther another roll of platinum gauze. After this is a third roll, and close beyond it the boat containing the sulphur compound. Last is a fourth roll of gauze. The bent end of the tube dips into water in a small flask, and the other end is closed with a stopper admitting the connecting tubes to the oxygen and nitric oxide supplies. After filling the tube with the mixed gases, the platinum roll on either side of the nitric acid boat is heated to low redness, then the boat farthest from the substance. This order of heating is particularly necessary when oxidizing substances that are easily volatile, as the primary oxidation products are very apt to strike back. The tube is then heated in the usual order of a combustion. The color of the tube between the two boats serves as an indicator: if the red color disappears the combustion must go more slowly. The nitric acid in the boat acts as a reserve; the hot gases in passing over it always take up enough oxygen compounds to complete the oxidation of any unburned particles. If the combustion goes slowly there is no appearance of flame, but it may be hastened considerably without danger. With aromatic substances, particularly naphthalene compounds, it may happen that the substance be converted into a nitro compound and

[1] Zeitschrift für analytische Chemie, **22**, 271. [2] *Ibid.* 177.

this then burnt like tinder; but even in such a case the oxidation is complete if there is sufficient nitric acid in the boat. At the end of the combustion the heating is extended forward until all the nitric acid, and the sulphuric acid formed in the reaction, have distilled over into the flask. After cooling, the contents of the flask and the washings of the tube are evaporated to dryness, and after dilution with water the sulphuric acid is determined as barium sulphate.

Nitric Acid.—C. Böhmer[1] describes a new method of estimating nitric oxide gas obtained by the reduction of nitric acid. Of the many methods that have been proposed for the estimation of nitric acid, those which are capable of the most extensive application, and which also yield the best results, depend on the reduction of nitric acid by ferrous chloride. Several processes have been used for carrying out this reaction. Pelouze treated the nitric acid with an excess of ferrous chloride and determined how much remained unaltered. C. D. Braun determined the amount of ferric chloride formed at the expense of the nitric acid, and finally Schlösing determined the quantity of nitric oxide formed by reconverting it into nitric acid, and F. Schulze recommended measuring the volume of nitric oxide itself. In an earlier paper[2] Böhmer has shown that chromic acid is an excellent absorbent for nitric oxide, and on this fact he now bases a method for determining the amount of gas yielded by nitric acid. The nitrate or nitric acid is decomposed in the usual way, and the resulting gas, after being dried by calcium chloride, is absorbed in a Liebig's potash bulb containing a concentrated solution of chromic acid, and the nitric oxide determined by the increase in weight.

Phosphoric Acid.—A new method for determining phosphoric acid in superphosphates, volumetrically, has been proposed by A. Mollenda.[3] The method consists in finding the amount of a standard solution of sodium carbonate necessary to neutralize the acid phosphate of calcium which forms the soluble portion of the superphosphate. In order to prevent the precipitation of calcium carbonate from any sulphate of calcium that may be present, the entire amount of calcium is precipitated by sodium oxalate and the acidity of the resulting mono-sodium phosphate determined. If there is free sulphuric or phosphoric acid in the superphosphate, sodium carbonate is added before titration until the liquid becomes slightly turbid.

Calcium and Strontium.—D. Sidersky[4] bases a method for the separation of calcium from strontium on the statement that on adding a mixture of sulphate and oxalate of ammonium to a solution of strontium, the latter is all precipitated as sulphate; on the other hand, if added to a solution of a calcium salt, only oxalate is precipitated. If the mixture is added to a solution containing both strontium and calcium, the former is precipitated as sulphate and

[1] Zeitschrift für analytische Chemie, **22**, 20. [2] *Ibid.* **21**, 212. [3] *Ibid.* **22**, 155. [4] *Ibid.* 10.

the latter as oxalate. The two precipitates are separated by the solubility of the oxalate in acids.

Preservation of Ferrous Sulphate.—A. Gawalovski[1] recommends placing a glass tube half filled with glass wool and an alkaline solution of pyrogallic acid in the crystals so that the mouth reaches somewhat above them. If the jar is then closed tightly the ferrous sulphate will remain unaltered for two or three years.

Copper and Zinc.—It has been shown by G. Larsen[2] that copper and zinc can be separated by one precipitation with hydrogen sulphide if hydrochloric acid is added to the solution of hydrogen sulphide with which the precipitate is washed. Emil Berglund[3] has studied this method independently, and finds that it holds good when a smaller amount ($\frac{1}{10}$ vol.) of hydrochloric acid is added to the wash water than recommended by Larsen, and further that zinc is not precipitated with copper if the amount of hydrogen sulphide in the wash water is small.

Titanium.—A method has been proposed by A. Weller[4] for the detection and estimation of titanium which is based on its reaction with hydrogen peroxide. When precipitated titanic acid is treated with a neutral solution of hydrogen peroxide, it changes to a lemon-yellow color; a concentrated acid solution of titanium gives a deep reddish-yellow color with hydrogen peroxide, without the evolution of any gas. This reaction is due to the formation of a higher oxidation product than titanic acid, and was announced by Schönn,[5] who recommended it as a characteristic test for hydrogen peroxide, but according to Weller the converse use furnishes a test for titanium compounds which is the most delicate known.

A few drops of hydrogen peroxide cause an orange-red coloration in a sulphuric acid solution of one milligram of titanic acid. With $\frac{1}{10}$ milligram the color is a distinct yellow, and even $\frac{1}{50}$ of a milligram can be detected. Tantalic and niobic acids and zirconium oxide, which often accompany titanic acid in minerals, give no similar reaction. The only substances which yield a similar color are vanadic and molybdic acids, and although in these cases the reactions are not so delicate, their absence must be insured in testing for titanic acid. In testing for very minute quantities of titanium, iron salts and other colored substances must of course be removed.

In order to use the reaction for estimating quantities of titanic acid, the depth of color is compared with solutions containing known amounts of titanic acid according to ordinary colorimetric methods. The great advantage of the method lies in the fact that it admits of the detection and estimation of titanic acid without the

[1] Zeitschrift für analytische Chemie, **22**, 33. [2] *Ibid.* **17**, 312. [3] *Ibid.* **22**, 185.
[4] Berichte der deutschen chemischen Gesellschaft, **15**, 2592.
[5] Zeitschrift für analytische Chemie, **9**, 41.

difficult separation from niobium and tantalum, and from zirconium, for which no exact method is known.

Vanadium.—A new method for the separation of vanadic acid from metals has been proposed by W. Halberstadt.[1] Like Classen's method for the separation of arsenic and phosphoric acids from the metals, it is based on the fact that when a mixture of the acid and metals is heated with ammonium oxalate and acetic acid, the metals are precipitated as oxalates while the acid sought for remains in solution.

The hydrochloric acid solution of vanadic acid is evaporated to dryness, the residue heated with a saturated solution of ammonium oxalate in water, and a few drops of strong acetic acid added till all has dissolved. The liquid is poured into a beaker and heated over a free flame, while acetic acid is added drop by drop until the precipitate ceases to form. If the acetic acid is added too rapidly the precipitate is difficult to wash. After filtering off the precipitate and washing with a mixture of equal parts of strong acetic acid, alcohol and water, the filtrate is evaporated to dryness in a weighed platinum dish, and the residue heated slowly to expel volatile ammonium salts, and then the remaining vanadium oxide is converted into vanadic acid by heating in a current of oxygen.

The method gives good results in presence of barium, calcium, zinc or lead, but not with cobalt, nickel, manganese, magnesium, bismuth, copper or cadmium.

Tungsten.—Otto F. von der Pfordten[2] has published a new method for the estimation of tungstic acid by reduction with zinc and hydrochloric acid to tungsten dioxide. The reduction takes place with more difficulty than the reduction of molybdic acid, and is best effected by using a 27 per cent. solution of hydrochloric acid. The solution first becomes blue, then a black-green, and finally a dark brownish-red, the end product being tungsten dioxide. This is determined by titration with potassium permanganate. If this is done in the usual way, results are obtained which correspond very nearly to a reduction to tungsten dioxide, but are never as high, because the solution is partially oxidized on exposure to air. But the results are quite exact if the titration is conducted according to Zimmermann's process: using an excess of permanganate, for which minute details are given in the original treatise. The method has one disadvantage, inasmuch as only very small quantities of tungstic acid can be used in the reduction, so that the percentage error may easily become large.

Illuminating Gas.—C. von Than[3] has invented a convenient instrument for estimating the amount of illuminating gas that may be present in the air in any confined space. The instrument is, in principle, a porous cylinder so arranged that the diffusion into it of any gas with a density different from air gives an indication on an open manometer.

[1] Zeitschrift für analytische Chemie, **23**, 1.
[2] Berichte der deutschen chemischen Gesellschaft, **16**, 508. [3] *Ibid.* **15**, 2790.

The Detection of Acetal.—M. Grodski[1] bases a method for detecting acetal on the fact that acetal itself gives no iodoform reaction; but when treated with an acid, both its decomposition products, alcohol and aldehyde, do yield iodoform when further treated with iodine in alkaline solution. By acidifying an aqueous solution of acetal with a few drops of hydrochloric acid, and adding caustic soda and a solution of iodine, the iodoform can be recognized even when 1 cubic centimetre of $\frac{1}{10}$ per cent. acetal solution is used.

Recent Investigations on Uranium.

Conclusive evidence as to the correct atomic weight of uranium has, until within the last year, been wanting.

As a result of the analytical investigations of Peligot, Wertheim and Ebelmen, the number 120 was for some time believed to be correct. Later, Mendelejeff called the attention of chemists to the fact that by assuming the correctness of the atomic weight 120, no suitable place could be assigned to uranium in his periodic scheme of the elements. This fact, together with a consideration of some of the properties of uranium, *e. g.* its high specific gravity, the difficult reduction of its oxides, the existence of a volatile chloride, etc., induced Mendelejeff to double the number heretofore accepted, thus placing uranium in the group including oxygen (typical), chromium, molybdenum and tungsten. To prove or disprove the correctness of his views Mendelejeff invited and recommended further investigation of uranium and its compounds.

Clemens Zimmermann[2] has responded to this invitation; and, in the first place by pointing out numerous analogies between compounds of uranium and those of chromium and other members of the same group, in the second place by directly determining the atomic weight to be 240, has justified the opinions of Mendelejeff.

The two fundamental oxides of uranium, namely the dioxide UrO_2, and the trioxide UrO_3, differ markedly, in that the former is strongly basic in character, while the latter possesses acid properties corresponding to the dioxide in the series of uranous salts, while the acid-forming oxide UrO_3 gives rise to the uranates.

In considering what place should be allotted to uranium in Mendelejeff's system, the following observation is of primary importance; *i. e.* while chromium, molybdenum and tungsten form well crystallised chromates, molybdates and tungstates, and not only normal (M_2XO_4; X = Cr etc.) but also poly-salts, heretofore only amorphous polyuranates have been prepared. Some of the experiments of Zimmermann had for their object to decide whether

[1] Berichte der deutschen chemischen Gesellschaft, **16**, 512.
[2] Annalen der Chemie, **213**, 285, and **216**, 1.

normal uranates could be prepared, and whether the normal or the diuranates were crystallisable.

Experiments were made on the alkaline uranates, the sodium, potassium and lithium salts being prepared and studied, great care being taken to secure the absolute purity of the substances considered. His results are as follows: Crystallised uranates were obtained; the potassium and sodium salts corresponded to the formula $M_2Ur_2O_7$, while the lithium salt answered to the formula Li_2UrO_4. These uranates have a beautiful orange-yellow color resembling that of powdered potassium dichromate; they are insoluble in water, easily soluble in dilute acids; when strongly heated they become like potassium dichromate, dark red, but on cooling resume their original color. Crystallographically considered they belong, according to Dr. C. Haushofer, to the rhombic or the clinorhombic system.

The normal lithium uranate differs from the potassium and sodium diuranates in the fact that when heated with water it decomposes into the hydroxides of lithium and uranium (uranyl hydroxide). Neither hot nor cold water has any decomposing effect upon the potassium and sodium diuranates.

These experiments show that the mono- and diuranates are analogous in composition and in a number of important properties to the corresponding compounds of chromium, molybdenum and tungsten, and thus one argument is produced in favor of placing uranium in the chromium group. Final evidence on this point can, however, be furnished only by direct determination of the atomic weight.

Zimmermann has observed the vapor densities of the chloride and bromide; in the case of the bromide the following data will serve to indicate the purity of the substance used:

Analysis of bromide:

	In 100 parts.			
	Found.		Calculated for $UrBr_4$.	
Substance used.	Br.	Ur.	Br.	Ur.
1. 0.2685	57.13	42.92	57.14	42.86
2. 0.3187	57.28	42.75	...	...
3. 2.3223	57.17	42.78	...	...

The vapor density was determined according to V. Meyer's method; the figures given below are the results of six determinations:

Vapor densities found, calculated on air as standard: (1), 19.50; (2), 19.33; (3), 19.34; (4), 19.58; (5), 19.44; (6), 19.58.

The mean of these figures is 19.46, which agrees well with the density 19.36 calculated for the formula $UrBr_4$ in which $Ur = 240$.

Equally satisfactory results were obtained in the case of the chloride, as follows:

Vapor densities found: (1), 13.24; (2), 13.36; (3), 13.40; (4), 13.31, giving the mean 13.3, which differs little from the value 13.21 calculated for the formula $UrCl_4$ ($Ur = 240$).

If, however, these halogen compounds contained in the molecule two atoms of uranium instead of one, the atomic weight of the element would be 120, and therefore additional evidence must decide whether 120 or 240 is to be preferred. This necessary evidence is furnished by the following determination of the specific heat of metallic uranium, Bunsen's ice calorimeter being employed. The mean of three determinations gave the figure 0.02765 for the specific heat. Multiplying this figure by 240, the atomic heat 6.64 is obtained, and this does not differ widely from the mean atomic heat, 6.4, of elements which conform to the law of Dulong and Petit.

The atomic weight 240 seems then to be firmly established, and the insertion of uranium into the chromium group no longer requires the aid of hypothesis.

In the course of these investigations Zimmermann has studied carefully the chemical conduct of the uranous salts, and finds that incorrect statements in regard to many reactions are to be found in the text-books. The uranous chloride and bromide in perfectly pure condition were used. The following statements give the results: the matter in parenthesis gives the reactions as heretofore accepted.

Potassium or sodium hydroxide produces in solutions of uranous salts a voluminous clear green (dark brown to blackish-brown) precipitate of uranous hydroxide, insoluble in excess of the reagent. This precipitate changes rapidly in contact with the air into brownish-black uranoso-uranic hydrate, which after some time becomes yellow potassium or sodium uranate.

Ammonia produces likewise a clear green, flocculent (dark brown) precipitate which undergoes the same changes as those produced by the fixed alkalies.

Secondary potassium or sodium carbonate causes the formation of a whitish-green precipitate, which by heating becomes dark in consequence of oxidation. Primary alkaline carbonates produce a similarly colored precipitate which easily dissolves in excess of the reagent, but by heating is again precipitated with partial oxidation.

Ammonium carbonate produces a whitish-green precipitate, easily soluble in excess and not precipitated again by warming.

Ferrocyanide of potassium creates immediately a yellowish-green (reddish-brown) precipitate, which gradually becomes reddish-brown in consequence of oxidation.

Ferricyanide of potassium effects immediately the formation of a reddish-brown precipitate (not immediately, but only after some time).

The addition of tartaric acid to solutions of uranous salts prevents the formation of a precipitate by ammonia, ammonium sulphide and fixed alkalies, the solution not becoming dark-colored (the solution is by such means colored dark or brown).

Ammonium sulphide causes a clear green precipitate, which rapidly becomes dark brown, and by heating black.

Barium carbonate precipitates uranous salts perfectly in the cold.

This series of investigations on uranium has been very fruitful in valuable results, among which may be mentioned, in addition to those already given, an important modification of the Margueritte method of determining iron, and also new methods of determining molybdic, tungstic and phosphoric acids, which methods have been fully worked out by certain other chemists associated with Zimmermann. W. C. D.

THE SYNTHESIS OF MINERALS AND ROCKS.[1]

The ideal development of almost any department of scientific inquiry may be divided into three distinct stages. The first period of simple observation is succeeded by one of analysis, while both are rounded out and completed by the final period of synthesis. In the case of the majority of the natural sciences it has thus far been possible to attain to only the first or second of these stages, but chemistry may boast that she has already made great progress into the third. What astounding results synthesis has yielded in the study of organic compounds is universally recognized, and to judge from the progress already made the inorganic field seems scarcely less promising.

Since the year 1801, when Sir James Hall succeeded in transforming common limestone into marble, there has been a continued effort to obtain by artificial means the minerals occurring in nature. These efforts have been attended by the most marked success, especially in France, where during this century wellnigh all the known mineral species have been successfully reproduced, the same result having often been attained by methods of the most diverse character. In the book before us the authors present a concise resumé of all that has thus far been accomplished by others in this direction, as well as many very interesting results of their own experiments in mineral synthesis, together with a complete bibliography of the whole subject. They have, however, not stopped here. Not being content with the reproduction of minerals as individual species, they have sought to combine them in their natural associations, thus imitating in the laboratory the processes of nature in the formation of the earth's crust. Here they were again successful, and by their experiments have thrown so much light upon questions of no less import to the chemist than to the mineralogist and geologist that it is to their detailed description (pp. 1–80) that the principal interest of the present work attaches.

The first chapter—*a General Introduction*—opens with a statement of five conditions which an artificial mineral product must fulfil in order to be a successful synthesis. 1st. It must be identical in its chemical composition with the natural mineral imitated. 2d. The two must also be crystallographically identical. 3d. Their

[1] Synthèse des Minéraux et des Roches, par F. Fouqué et A. Michel-Lévy. Paris, 1882.

internal structure, *i. e.* cleavage, inclusions, etc., must be the same. 4th. The artificial minerals must follow the same laws of association as the natural ones. 5th. The conditions of the artificial operation must be compatible with the circumstances under which the natural products were formed.

These conditions are followed by a classification of syntheses into intentional and accidental, which in turn is succeeded by an enumeration of several causes to which, during late years, the rapid advancements made in rock synthesis have been largely due. These are: 1st. The introduction of the microscopical examination of rocks, whereby the relative age of the mineral constituents has been revealed, and thus many valuable hints obtained as to the mode of operation, as well as a means of accurately studying the products. 2d. The recent improvements in laboratory appliances. 3d. The gradual overthrow of the traditional idea that the methods of nature are altogether inscrutable, and that any imitation of results accomplished by the joint agency of indefinite time and enormous pressure is out of the question in the laboratory.

Various ways in which synthesis has been of special utility in the study of natural products, by the interpretation of obscure facts, etc., are then noted, while the chapter closes with a classification of all the methods thus far employed in the artificial reproduction of inorganic bodies, as follows:

I. Those producing a molecular change in *solid* bodies.

(*A*) Without chemical action, *e. g.* monoclinic sulphur changing to rhombic.

(*B*) With chemical action, *e. g.* marble produced from limestone.

II. Those producing a molecular change in *fused* bodies.

(*A*) Without chemical action.

(1) Without a solvent, *e. g.* fused silicates, as felspar.

(2) With a solvent, *e. g.* carbon changed to graphite in melted iron.

(*B*) With chemical action, orthoclase, etc., from alkaline tungstates and vanadates.

III. Those producing a molecular change in *volatilised* bodies.

(*A*) Without chemical action, *e. g.* sublimation.

(*B*) With chemical action.

(1) The mutual chemical reaction of vapors, *e. g.* steam and iron chloride forming iron oxide.

(2) The action of vapors on a solid body, *e. g.* zircon and corundum, formed by a gas acting as a "*minéralisateur*."

IV. Those producing a molecular change in bodies *dissolved* in water.

(*A*) At ordinary pressure.

(1) By evaporation, *e. g.* salt and gypsum.

(2) By a supersaturated solution.

(3) By variations of temperature.

(4) By chemical reactions.

(*B*) Under high pressure, *e. g.* quartz.

V. Molecular changes produced by a combination of any of the above processes.

The crystalline constituents of the earth's crust are then arranged for purposes in hand in four categories:

1st. The minerals of volcanic rocks, *i. e.* basic (plagioclase) rocks.

2d. The minerals of acidic rocks, *i. e.* quartz and orthoclase rocks.

3d. The minerals of the crystalline schists, *e. g.* gneiss and mica-schist.

4th. Mineral veins.

Now the following statement sums up in a word all we thus far know of mineral and rock synthesis: *The minerals and their associations of the first of these four categories have nearly all been artificially reproduced by simple fusion; those of the last by solution or volatilisation. Those of the two remaining categories have, on the contrary, not yet been artificially obtained.*

The second chapter on the *Artificial Reproduction of the Eruptive Rocks* contains a detailed account of the methods employed and the results obtained by the authors themselves, preceded by a brief notice of experiments previously made by others in this direction.

Daubrée, Vogelsang, Friedel and Saracin all attempted to reproduce quartz and orthoclase by means of superheated alkaline solutions without decided success. Hautefeuille obtained these minerals crystallised out of fused tungstates, vanadates and phosphates of the alkalies; but this method, interesting in itself, throws little light on their geological genesis. Experiments with simple fusion were performed by Sir James Hall (1801), Gregory Watt (1804), Daubrée (1866), and Sorly as late as 1880, leading, however, only to the conclusion that this was *not* the method of nature in the formation of her lavas. The field was therefore practically new when Fouqué and Lévy entered it in 1878.

The apparatus employed by these investigators was comparatively simple, consisting of a furnace of moderate dimensions by Leclerc and Forquignon, heated by a blowpipe supplied by ordinary illuminating gas and driven by a Damoiseau blast. This arrangement was found to fulfil very satisfactorily the two necessary conditions by readily furnishing a high temperature and allowing the same to be maintained for a considerable time. The substances to be fused (either the fundamental chemical constituents of the desired product or pounded minerals) were placed in a very finely divided and well-mixed state in platinum crucibles, which were encased in coverings of fire clay. By properly regulating the furnace any degree of temperature could be obtained at will. Four grades most frequently employed are designated as temperatures Nos. 1, 2, 3, 4, as follows:

No. 1. The temperature of fused platinum; also sufficient to reduce anorthite, leucite and olivine to a vitreous mass.

No. 2. The melting point of steel, where all the felspars except anorthite are fusible.

No. 3. A temperature between the melting points of steel and copper. Pyroxene and nepheline fuse readily.

No. 4. The melting point of copper.

All rock-making minerals when fused and rapidly cooled give a perfectly homogeneous isotropic glass, Some, however, crystallise much more readily than others; for instance, it was necessary to cool the molten mass very rapidly to prevent pyroxene, enstatite, melilite and nepheline from crystallising, while the felspars required a much longer time to complete their regular molecular arrangement.

After a certain amount of experience had been obtained with the reproduction of individual minerals, their associations were secured by the employment of a principle, already well known to Hall, that *the melting point of a crystallised silicate is in general higher than that of the same chemical compound in an amorphous state.* If, therefore, the molten mass be held for a time at a temperature between the melting point of the least fusible mineral and its glass, this mineral will crystallise out, and then, if the temperature be lowered to just the right point, the next more easily fusible mineral may be obtained in the same way, and so on to the most easily fusible. It is then a general *rule* that the minerals must crystallise out of a molten magma in the inverse order of their fusibilities. This is mostly the case, but occasional apparent *exceptions* deserve to be noticed and explained.

1st. Certain minerals whose point of fusion is very high, as for example leucite, often contain inclusion of much more easily fusible minerals. The explanation here is that these were included as portions of the amorphous magma, which afterwards by a lower temperature assumed a crystalline structure.

2d. Magnetite, and often picotite, appear as inclusions in silicates of two different periods of crystallisation. The explanation of this fact seems to be that certain bases mutually react and change places, so that the fusibility of these minerals is *not* a function of their time of crystallisation.

3d. The most important exception is that certain *silicates* appear in two successive periods or generations, *e. g.* pyroxene and labradorite often appear both as porphyritic crystals and as microliths in the ground mass. The distance between the points of fusibility of a mineral and its glass may be so great as to allow of its crystallising in two periods, *e. g.* a period of very slow cooling before the eruption of a volcanic rock and the period of rapid cooling immediately succeeding its eruption.

In practical experiments it was found that at temperature No. 2, crystals of leucite, anorthite, olivine, magnetite and picotite were obtained; at temperature No. 3, crystals of labradorite, oligoclase, pyroxene, enstatite, hypersthene, and also magnetite and

picotite; at No. 4, crystals of the same minerals, but especially pyroxene, nepheline, melilite and melanite.

The methods for examining these artificial products are in all respects identical with those employed in the science of petrography for the examination of natural rocks.

By judicious combinations of the methods already recounted the authors have thus far succeeded in obtaining eleven distinct mineral associations or rocks, almost exactly reproducing, even in the minutest details of structure, as many widespread natural types.

I. *Andesites.* Mixture: 1 part augite to 4 parts oligoclase, or its equivalent in chemical substances. This was held for three days at temperature No. 3. *Result:* microliths of oligoclase .25 mm. × .015 mm., of augite .06 mm. × .02 mm. arranged without order and a little magnetite in octahedrons.

II. *Labrador Andesites* ("Labradorites"). Mixture: 1 part augite to 3 parts labrador. Temperature and time as in I. The microliths of labrador and augite are larger and stouter. Twins of the former according to the albite law very common. Magnetite much more abundant than in I.

III. *Anorthite Augite Andesite.* Rare in nature, but obtained artificially without difficulty.

IV. *Basalt and Labrador melaphyre.* Two successive stages of fusion at different temperatures were necessary for the production of this rock. A mixture equivalent to 6 parts olivine, 2 augite and 6 labrador was kept for 48 hours at temperature No. 2, *i. e.* above the fusing point of labrador and augite. The product was numerous crystals of olivine, of the usual natural appearance, averaging .5 × .2 mm., imbedded in an isotropic amorphous glass. This was again subjected to temperature No. 4 for 48 hours, when the glassy base was completely transformed into microliths of labradorite and augite. Magnetite and picotite were formed during both stages of fusion.

V. *Nephelinite.* Mixture: 3 parts nepheline to 1.3 of augite. Temperature No. 4, 48 hours; association hexagonal prisms (.02 mm.) of nepheline with microliths (.01 × .004 mm.) of augite. A mixture of 10 parts nepheline and 1 of augite produced, when treated in the same manner, crystals of nepheline, spinel and black garnet (melanite).

VI. *Leucitite.* Mixture: 9 parts leucite and 1 of augite. Temperature No. 2; 3 days. It was not necessary to fuse twice, notwithstanding the ease with which augite melts, because this mineral crystallises so readily and rapidly.

VII. *Leucite tephrite.* A mixture of silica, alumina, potash, soda, magnesia, chalk and iron oxide, equivalent to 8 parts leucite, 4 of labrador and 1 of augite, was fused into a homogeneous glassy mass. This was subjected in successive stages to temperature No. 2 (48 hours); and temperature No. 4 for the same time. During the first stage of the process the leucite, magnetite and picotite crystallised out of the magma. What remained was converted

during the second stage into a crystalline groundmass of labrador and augite microliths.

VIII. *Lherzolite.* This rock was produced first by Daubrée in 1866. By a more prolonged cooling the enstatite forms short prisms instead of long needles. However, the rock does not exhibit precisely the same structure as that found in nature. Thus the picotite is in small octahedrons instead of irregular masses, and glass inclusions are much more numerous.

IX. *Meteorites without Felspar.* Two types were reproduced:

1. Kragujewatz type. Olivine, enstatite, magnetite, native iron.

2. Rittersgrün type. Olivine, magnesian pyroxene, enstatite, native iron.

(1) 12 gr. SiO_2; 3 gr. MgO; 5.55 gr. Fe_2O_3; temperature No. 3 for 3 days.

(2) 6 gr. SiO_2; 3 gr. MgO; double sulphate of iron and ammonia corresponding to 1.8 gr. Fe_2O_3.

A pure magnesium diopside already obtained by Ebelmen is most interesting.

X. *Felspathic Meteorites.* 1 *Eukrites:* anorthite, enstatite and pyroxene; and 2, *Howardites:* anorthite and olivine, both successfully obtained.

XI. *Diabases and Dolerites with ophitic structure.* The difficulty here was to obtain elongated crystals of felspar entirely surrounded by irregular masses of homogeneous pyroxene. It was wellnigh impossible with oligoclase or labrador, whose fusing points are so near that of pyroxene. With anorthite, however, this difficulty disappears. A mixture of equal parts of both minerals subjected to temperature No. 2 four days, and as long to temperature No. 3, gave the required result. In case temperature No. 4 is used, a union of the ophitic and microlithic structure is observed in the same slide.

Experiments productive of no positive results. All attempts to reproduce rocks containing quartz, orthoclase, albite, muscovite, biotite, or amphibole by fusion have proved unsuccessful. These minerals when melted give either an amorphous glass or pass into other combinations giving rise to minerals already produced; *e. g.* hornblende changes to pyroxene.

In this way the *general important result* was obtained that the *acidic rocks*, i. e. *those containing the minerals above named, owe their origin to some other means than igneous fusion.*

G. H. WILLIAMS.

RECENT APPLICATIONS OF THE PRODUCTS OF COAL-TAR DISTILLATION.

The practical applications of the results of investigations in pure chemistry are nowhere better shown than in the utilisation of coal tar, especially in the manufacture of the almost innu-

merable organic coloring matters. Within recent years this branch of industrial chemistry has made enormous progress. The activity of chemists has been exerted to a much higher degree in developing the applications of the direct products of tar distillation than in bettering the methods of obtaining these products. Comparatively little improvement has been made of late in the construction of tar retorts and in the methods of tar distillation. Distillation under diminished pressure,[1] in order to obtain the high boiling compounds at a lower temperature, is gradually coming into vogue, although it leads to little or no improvement in the purity of the distillates. On the contrary, distillation with the aid of superheated or spent steam, as practised at La Villette where the Paris gas tar is worked up, is but little used elsewhere. In recent years, several of the coal-tar hydrocarbons have found extensive practical application in the manufacture of the azo colors. The azo compounds, containing the group $-N=N-$ in combination with two aromatic nuclei, are all colored, but the azo hydrocarbons themselves have no affinity for animal and vegetable fibres, and hence cannot be used as dyes. On the other hand, such of their derivatives as contain amido or hydroxyl groups are coloring matters. Some of these have long been known, but with the exception of aniline yellow (oxalate or hydrochlorate of para-amidoazobenzene, $C_6H_5.N=N[1]C_6H_4[4]NH_2$), and Bismarck brown (hydrochlorate of triamidoazobenzene, $C_6H_4\begin{cases}[1]NH_2\\[3]N=N[1]C_6H_3\end{cases}\begin{cases}[2]NH_2\\[4]NH_2\end{cases}$) the azo compounds were not made use of until 1876. Since then, and especially since 1878, a great number of new ones have been made, many of which have been patented and manufactured on a large scale.

The oxyazo colors are made from a diazo salt and the compound of a phenol with an alkali metal, *e. g.*:

$$C_6H_5N=NCl + C_{10}H_7OK = KCl + C_6H_5N=NC_{10}H_7OH.$$

The colors may be prepared separately or developed directly upon the fabric from the appropriate substances.

The amidoazo colors are made on a large scale by the action of nitrous acid ($NaNO_2$ and HCl) on a free amine, or where this is not practicable, as when a diazoamido compound would be formed, or when a substance containing different hydrocarbon radicals is desired, by the action of a diazo salt on an amine, *e. g.*

$$C_6H_4\begin{cases}SO_3H\\N=NCl\end{cases} + C_{10}H_7NH_2 = C_6H_4\begin{cases}SO_3H\\N=NC_{10}H_6NH_2HCl.\end{cases}$$

By means of these reactions the number of azo colors which may be formed from aromatic compounds containing amido and hydroxyl groups is almost infinite. When benzene and toluene were used almost solely for the production of the colors of the tri-

[1] Chemiker Zeitung, 3, 146.

phenylmethane group, the quantity obtained from gas tar was fully equal to all demands. Since the azo colors were introduced their popularity has become so great that the demand for the hydrocarbons used in their manufacture has increased greatly, and the price of these compounds is much higher than formerly. To obtain a greater supply of the hydrocarbons the attempt has been made, both in the Caucasus and in America, to make them by distilling petroleum residues through iron tubes loosely filled with bricks and heated to redness, whereby the paraffins are partially transformed into hydrocarbons of the aromatic group. This has not as yet proved a commercial success, as very extensive apparatus, requiring a large outlay of capital, is needed for working it on a large scale. It is also proposed to introduce petroleum residues into the tar retorts after the distillation is nearly completed, and then to distill again. It is, however, doubtful whether, with the ordinary tar apparatus, sufficient transformation could be obtained, especially as the separation of the aromatic hydrocarbons from the fatty hydrocarbons of nearly the same boiling points is a difficult matter. For the manufacture of azo colors practically pure benzene is required, since even small quantities of its homologues may seriously interfere with the purity of the colors. The separation of the constituents of the light oils, benzene, toluene, the xylenes, and other homologues is now almost exclusively carried on in stills like those used for distilling alcohol, consisting of a boiler provided with a vertical column many feet high, divided into compartments partially separated by horizontal partitions, and cooled by air, thus admitting of fractional condensation. By this means nearly pure products are obtained by one distillation.

The synthesis of indigo seemed to promise a great demand for toluene. The preparation of artificial indigo, however, while offering some advantages over the use of the natural product, has not been able to compete successfully with the latter. The study of the indigo group is being vigorously carried on, and the time may not be distant when the artificial product may replace the natural as completely as artificial alizarin has replaced that extracted from madder.

At present toluene is mostly used for making rosaniline, benzoic acid, azo colors and benzaldehyde. The last is used in the preparation of the important malachite green. This color has the composition $3(C_{23}H_{24}N_2) + 2ZnCl_2 + 2H_2O$. At the works of Meister, Lucius and Brüning in Höchst, it is thus prepared: 1 mol. benzaldehyde and 2 mols. dimethylanilin are condensed by heating with zinc chloride, the reaction being

$$C_6H_5CHO + 2C_6H_5N(CH_3)_2 = H_2O + \underbrace{C_6H_5CH\begin{cases}[1]\,C_6H_4\,[4]\,N(CH_3)_2\\[1]\,C_6H_4\,[4]\,N(CH_3)_2\end{cases}}_{\text{Tetramethyldi-p-amidotriphenylmethane.}}$$

This leuco-base, by oxidation with chloranil, loses two hydrogens, giving

$$C_{23}H_{24}N_2 = C_6H_5C\begin{cases}[1]C_6H_4[4]N(CH_3)_2\\ [1]C_6H_4[4]N\,CH_3\\ \qquad\qquad\quad CH_2\end{cases}$$

which in combination with zinc chloride forms malachite green.

The three nitrobenzaldehydes also form condensation products with the aromatic amines by action of zinc chloride, giving various substituted nitrodiamidotriphenylmethanes, leuco-bases which either by direct oxidation or oxidation after reduction of the nitro group, yield the bases of various coloring matters. Thus paranitrobenzaldehyde and aniline give a nitrodiamidotriphenylmethane, which, after reduction of the nitro group, can be oxidised to pararosaniline. A method which would enable us to obtain paranitrobenzaldehyde cheaply and of sufficient purity would perhaps make a revolution in the methods of manufacturing the rosaniline colors.

Xylene finds application in the manufacture of certain red azo colors. The xylidine used for this purpose is made from crude nitroxylene, which is prepared from crude xylene, a mixture of o- m- and p-xylenes. Crude xylidine has also been applied recently in the synthesis of so-called cumidine, amidopseudocumene, from which azo colors are made. It is obtained by heating a mixture of crude xylidine hydrochlorate and methyl alcohol to 230° C. under pressure. Methylxylidine hydrochlorate and water are thus formed, but at this temperature, according to the principle discovered by Hofmann and Martius,[1] the methyl passes into the aromatic part of the molecule, forming amidopseudocumene. Martius has recently isolated from the crude mixture thus obtained a new crystallised cumidine, from which azo colors may be made.

Pure naphthalene is now prepared on a large scale and used for making azo colors, while formerly it was used only for making phthalic acid, which found application in the manufacture of the phthalein colors. The naphthalene azo colors are made from the naphthylamines and naphthols and their derivatives, especially the naphthol mono- di- and trisulphonic acids. Many of these are manufactured on a large scale, especially in Germany. Among the most important of these colors is crocein scarlet, the sodium or sodium-ammonium salt of the compound

$$C_6H_4\begin{cases}[1]SO_3H\\ [4]N=N[1]C_6H_4[4]N=N.C_{10}H_5\end{cases}\begin{cases}[\alpha]SO_3H\\ [\beta]OH\end{cases}.$$

α-Naphthylamine is made for practical purposes by reduction of α-nitronaphthalene. β-Nitronaphthalene being unknown, the β-amine could be prepared only indirectly and with difficulty until Caro[2] obtained it by the action of ammonia on β-naphthol at 150°–160° C., some of the secondary amine being also formed.

[1] Berichte der deutschen chemischen Gesellschaft, **4**, 742. [2] *Ibid.* **14**, 1589.

About the same time Merz and Weith[1] found that by heating β-naphthol with ammonio-zinc chloride to 200°–210° C., the primary and secondary β-naphthylamines are formed, the latter, however, in much greater quantity. More recently Benz[2] has found that by using ammonio-calcium chloride, the primary amine is formed in much greater amount than the secondary amine. Benz also found that the α-amine could be similarly prepared from α-naphthol. Whether the β-amine can be practically prepared by Benz's method remains to be seen. It is not probable that his method of making the α-amine will ever replace the old method of reduction of α-nitronaphthalene.

But little progress has been made of late years either in the preparation or application of anthracene. Its quality has even degenerated rather than improved. Instead of boiling the tar down only to soft pitch, as was customary about fourteen years ago, it is now common to continue the distillation until hard pitch is obtained. While more anthracene is thus obtained, it is relatively more impure, being contaminated with larger quantities of the higher boiling hydrocarbons, from which it is separated with difficulty, and which are prejudicial to its use.

Of the innumerable compounds which exist in coal tar, the only ones which are at present extracted for practical purposes are benzene, toluene, xylene, naphthalene, anthracene, phenol and the cresols; the hydrocarbons chiefly for the color industry, and the phenols for disinfecting and antiseptic purposes. Phenol is also largely used in making salicylic and picric acids and some azo colors. Other useful ingredients of tar are at present more profitably manufactured by indirect methods.

Some of the substances occurring in abundance in tar have as yet been put to no practical use, as phenanthrene and other high boiling hydrocarbons, and carbazol. Phenanthrene, obtained as a residue in the purification of anthracene, is used for little else than making lampblack. It has also been used to replace oil in oil baths, but owing to its comparative volatility it is objectionable. Eugen Fischer[3] obtained from resorcin and phenanthrene-disulphonic acid a yellow dyestuff. Anschütz and v. Siemienski[4] have made a red azo color from diazobenzene-sulphonic acid and phenanthrol. The anhydride of diphenic acid $\left.\begin{matrix} C_6H_4CO \\ C_6H_4CO \end{matrix}\right\rangle O$, obtained by oxidising phenanthrenequinone, forms with phenol and resorcin colored compounds analogous to the phthaleins.[5] As yet, however, phenanthrene, although readily obtained in pure condition, has not been employed in the color industry.—(*Based upon an article in the Chemiker Zeitung*, **7**, 371 *and* 387.) H. N. S.

[1] Berichte der deutschen chemischen Gesellschaft, **13**, 1300.
[2] *Ibid.* **14**, 2344; **16**, 8. [3] *Ibid.* **13**, 314. [4] *Ibid.* **13**, 1180.
[5] Graebe and Mensching, *Ibid.* **13**, 1304.

On the Inconstancy of the Atomic Weights.

After the admirable investigations of Stas on chemical proportions it would seem almost presumptuous to call in question the accuracy of the law of definite proportions. Schützenberger,[1] in analysing the petroleum of the Caucasus, frequently obtained 101 to 101.5 per cent. of carbon and hydrogen. In seeking an explanation of this, he claims to have observed that if the petroleum, or pure benzene or aniline be distilled over sodium or copper, they acquire the property of giving more than 100 per cent. on analysis. If kept in the dark they retain it for a long time, but exposure to the light destroys this property, and, when analysed after such exposure, they gave 100 per cent. The analyses, he states, were made with the greatest care, and he is unable to account for the anomaly otherwise than by supposing that the composition of water and carbon dioxide varies within certain narrow limits, or that the atomic weights are not always constant.

Butlerow,[2] speaking of Schützenberger's observations, also regards with favor the idea that the atomic weights are variable. The atomic weights, he holds, although they cannot be expressed in whole numbers, approach in so many cases to whole numbers that it can hardly be attributed to accident. The hypothesis of Prout is, therefore, not altogether without foundation, which conclusion was also reached by Mallet and Clarke. Empirical data, from which is deduced a general law which can be expressed in a simple and rigid way, do not exactly correspond with such a law, but vary within certain limits, according to the conditions of the experiment. For example, Boyle's or Marriotte's law. Hence, Butlerow raises the question whether under certain conditions Prout's hypothesis does not actually represent the truth, and therefore concludes that on this basis the absolute constancy of the atomic weights might be denied. In a subsequent communication[3] Schützenberger mentions the observations which led him to assume that the law of definite proportions is not absolute. Barium carbonate, prepared by precipitating pure baryta water with carbon dioxide at the boiling temperature, contains, if it is first dried at 110° and then at 440°, 21.7 per cent. CO_2 and 78.5 per cent. BaO. If the carbonate is then heated in a current of oxygen to red heat it increases in weight without losing carbon dioxide; the product contains 22.0–22.05 per cent. CO_2, and 76.5 per cent. BaO. Hence barium carbonate has the power of fixing oxygen, which has increased the relative weight of carbon dioxide. Carbon monoxide was passed over a weighed quantity of copper oxide at a red heat, the carbon dioxide and reduced copper determined. The weight of copper oxide, minus the weight of the copper found, gave the weight of oxygen used, and the weight of carbon dioxide found, minus the weight of oxygen used, gave the weight of carbon monoxide

[1] Chemical News, **45**, 50.
[2] Journal der russ. phys. chem. Gesellsch. 1882, 208.
[3] Bull. Par. **34**, 268.

consumed. The ratio CO : O was found to be 14 : 8.05, instead of 14 : 8. Hence, one equivalent of carbon monoxide can take 8.05 parts of oxygen from copper oxide. In making syntheses of water he obtained results, according to which the ratio O : H varied between 7.95 and 8.15. In other cases the variation was still greater, and as he could obtain no constant ratio he concludes that the composition of the water formed varies with the condition of the copper oxide, the length of time it is in contact with it, and temperature at which it is formed! By numerous other analyses he claims to have shown that the composition of many metallic oxides varies within certain limits which depend upon the methods of their formation.

Schützenberger has not published the details of his experiments, nor given a description of his apparatus. It should be stated further that the idea of the variableness of chemical composition is not original with him. Marignac[1] in 1860 raised the same question which Schützenberger now raises, and it led Stas to carry out his admirable investigations on the laws of chemical proportions, in which, by the most accurate experimental methods, using every imaginable precaution to avoid error, he succeeded in showing that, under all conditions of temperature and pressure, bodies combine in absolutely fixed and unchangeable proportions,[2] that these proportions are real constants, that the laws of chemical combination are mathematically exact and not mere approximations which hold within certain limits. E. H. K.

NOTES.

On the Properties of Antiseptics and of the Volatile Products of Putrefaction.

M. GUSTAVE LE BON has recently been carrying on investigations upon the action of antiseptics, the results of which have led him to the following conclusions:

1. The disinfectant power of any antiseptic is the more feeble as the putrefaction is the more advanced. If for a normal liquid there be taken an aqueous solution containing a tenth of its weight of minced meat, this solution will exhale during the first stages of putrefaction an extremely fetid odor, which, however, can be destroyed by a comparatively small amount of antiseptic. At the end of about two months new bodies with a special odor will be

[1] Bibliothèque universelle de Genève, **9**, 97. [2] Stas. Chemische Proportionen, 15–108.

developed, which, contrary to what might be supposed, can only be destroyed by quantities of the same antiseptic at least twice as great as at first.

2. If the power of antiseptics be measured by taking as a means of comparison their disinfectant properties upon a given weight of the normal solution mentioned above, it will be seen that the most powerful disinfectants are potassium permanganate, "chloride of lime," sulphate of iron acidified with acetic acid, phenol, and the glyceroborates of sodium and potassium. To disinfect, for example, 10 cc. of the normal solution will require 500 cc. of a saturated aqueous solution of salicylic acid, 80 cc. of a saturated solution of phenol, 80 cc. of a ten per cent. solution of glyceroborate of sodium, and only a few drops of a one per cent. solution of potassium permanganate.

3. There is no parallelism between the disinfectant action of an antiseptic and its action upon microbes. Potassium permanganate, which is one of the most powerful disinfectants, exercises no appreciable action upon microbes. Alcohol, which on the contrary checks their development, exerts only a very feeble disinfectant action upon the products of putrefaction.

4. There is likewise no parallelism between the power of preventing putrefaction and that of checking it when it has begun. Phenol and alcohol, which are excellent preservative agents, have but a slight action upon putrefaction when it has begun, and if phenol is so useful in surgery, it is solely as a preventive agent.

5. With the exception of a very few substances which are powerful toxic agents, such as mercuric chloride, the greater number of antiseptics, and notably phenol, have only a very feeble action upon bacteria. If 10 cc. of the normal solution mentioned above be mixed with 50 or even 100 cc. of a saturated aqueous solution of phenol, the larger bacteria are made motionless, but the smaller remain in full activity, and may be perfectly reproduced by cultures. M. Le Bon even considers phenol as one of the best liquids which can be employed to preserve living bacteria for a long time.

6. The experiments made upon cadaver alkaloids cannot serve to decide the question as to whether the volatile alkaloids, which give to putrefaction its odor, are poisonous, for such experiments have generally been made by introducing into the system putrefaction products containing bacteria, to which the effects observed may be attributable. The method of experimenting adopted by M. Le Bon has been simply to place frogs in jars, in the bottom of which there is a very thin layer of the normal liquid already mentioned. Under these conditions it was noticed that at the beginning of putrefaction the liquid, although rich in sulphuretted hydrogen, possessing an extremely fetid odor, swarming with bacteria, and, as is known, very virulent if injected under the skin, had no appreciable effect upon the animals placed in the jar. On the other hand, the same liquid, two months old, and, as is

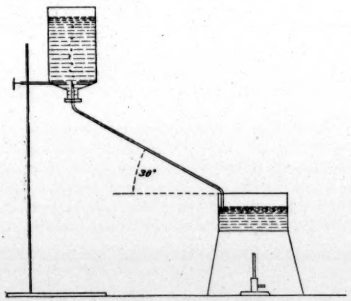
also known, no longer having virulent properties, kills in a few minutes the animals which breathe its exhalations. There is then no parallelism between the virulent power of a body in putrefaction and the toxic power of the volatile compounds which it gives off. These two properties even seem to be in inverse ratio to each other.

7. The extremely minute quantity of the products of advanced putrefaction necessary to kill an animal by simple mixture with the air which it breathes, shows that these volatile alkaloids are extremely poisonous, and experiments involuntarily made upon himself by M. Le Bon during the course of his investigations indicate that they are equally poisonous to man. M. Le Bon states that he knows of but very few bodies, such as nicotine, prussic acid, and the new alkaloid extracted by him from tobacco, which are equally poisonous.

8. The preceding experiments explain the accidents which have accompanied the exhumation of bodies interred for a long time, and prove that the atmosphere of cemeteries may, contrary to what has been stated judging by its freedom from microbes, be very dangerous. The volatile alkaloids engendered by the action of microbes upon certain organic substances play, beyond doubt, an important role in very many affections.—(*Comptes Rendus*, 95, 259.) R. D. C.

Constant Water-Bath.

The following simple form of constant water-bath, which wastes no water, I have found to be very convenient:



A tube of glass or metal, not less than one-quarter of an inch internal diameter, the ends of which are cut off obliquely, is bent as shown in the cut. It should make an angle of about 30° or a little greater with the horizontal. The angle may be diminished if

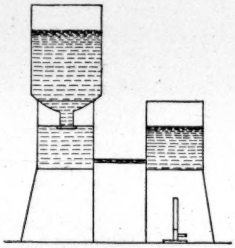
the bore of the tube is increased. One end is inserted in the water-bath, the other in an inverted bottle. The height of the water in the bath is regulated by the depth of immersion of the tube in it. The boiling is not interrupted by the feeding, which takes place slowly and regularly. It is necessary that the ends of the tubes should be cut off obliquely. The same form of tube answers equally well for keeping a constant level in a filter or drying chamber.

A brass tube is much better than a glass one, as it does not crack at the water-level after using for a time. Brass tubes can easily be bent by ramming full of sand, stopping the ends and bending them over a curved surface. A large number of baths can be run by this apparatus by connecting them with a bath fed by it.

CHARLES T. POMEROY.

NOTE.—We have used for a number of years in this laboratory a form of constant water-bath which was contrived by Mr. Edward Bogardus, formerly chemist to the N. J. State Geological Survey. As I have not seen it described in print, and as it is cheap, simple, efficient and ingenious, I will draw attention to it here.

The following cut represents the apparatus:



It consists of two tomato cans connected by a tin tube. Into one of the cans a bottle of water is inverted. We generally use a five-pound acid bottle. The other can makes the bath. This bath can be left running over night without fear. A large number of baths can be run by this contrivance by simply connecting them by means of rubber tubes, with a reservoir replenished by an inverted bottle. Old fruit cans make excellent baths. A series of holes can be punched round the lower edge of a fruit can, thus affording a distributing reservoir. Corks holding short pieces of glass tube are inserted into the holes. By means of these the reservoir can be connected by rubber tubes with a number of baths at quite a distance. The baths are made by punching a hole near the lower edge of a fruit can and inserting a cork and short piece of glass tube. When the extra vents of the reservoir are not used they can be closed by a short rubber coupling and a pinch-cock.—[PETER T. AUSTEN, Chemical Laboratory of Rutgers College (N. J. State Scientific School).

Separation of Sugar from Molasses and Syrups by means of Strontium Saccharate formed at low temperatures.

The process here described was devised by Dr. C. Scheibler, of Berlin. If strontium hydroxide be added to a 20–25 per cent. solution of sugar at a temperature of 70–75° C. in the proportion of one molecule of $Sr(OH)_2.8H_2O$ to one molecule of $C_{12}H_{22}O_{11}$, there is formed a strongly supersaturated solution of monobasic

strontium saccharate. The warm concentrated solution, if protected from the carbon dioxide of the air, and allowed to cool to ordinary temperatures, remains unchanged for some time without anything separating. It is possible to obtain either strontium hydroxide or monobasic strontium saccharate from it accordingly as we add crystals of one or the other substance to the solution. The monosaccharate by this means can be obtained in the form of a white granular powder having the composition represented by the formula $C_{12}H_{22}O_{11}SrO.5H_2O$. These facts have found practical application in a method for the extraction of sugar from molasses and syrups. The molasses whose percentage of sugar is approximately known is diluted with water and heated to boiling, a solution of strontium hydroxide of known strength is then added until for each molecule of sugar present one and a quarter molecules of $Sr(OH)_2.8H_2O$ have been added. The liquid is then allowed to cool to ordinary temperatures, and a few crystals of strontium monosaccharate added. At once the crystallisation of this compound begins and continues for 12 to 24 hours. In this way two-thirds to three-fourths of the sugar in the solution is removed. The mono-saccharate is separated from the mother-liquor in the usual way by means of filter-presses, centrifugals, etc. The strontium saccharate is then suspended in water and decomposed by carbon dioxide. After filtration there remains a solution of sugar free from strontium, from which crystallised cane sugar is obtained by evaporation.

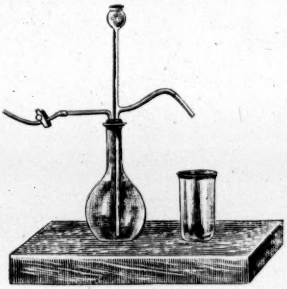
The mother-liquor separated from the crystals of monosaccharate still contains from one-fourth to one-third of the original quantity of sugar present in the molasses. To recover this the liquid is boiled for a long time with an excess of strontium hydroxide; all the sugar is thus precipitated as bibasic strontium saccharate. The liquor is decanted from the bisaccharate and the excess of strontium recovered by allowing it to cool, when a portion crystallises as strontium hydroxide; the remainder is precipitated with carbon dioxide. The residual liquid free from sugar and strontium leaves the factory to be used as a fertiliser, or is worked up for the potassium salts, ammonia, etc., which it contains.

The bibasic strontium saccharate is added to the next portion of molasses to be treated; it dissolves readily, forming monosaccharate, because of the excess of sugar present. When completely dissolved the hot concentrated solution of molasses is treated with a warm solution of strontium hydroxide of known strength, until the molecular relation between the total quantity of sugar (sugar of the molasses and sugar of the bisaccharate) is to the strontium hydroxide as 1 to 1½. The liquid is allowed to cool and the monosaccharate separated as before. By operating in this way all the sugar in molasses or syrups may be obtained as monobasic strontium saccharate, which is easily decomposed into strontium carbonate and pure sugar.—(*Chemiker Zeitung*, 1883, **7**, 420.)

E. H. K.

A New Gas Generator.

The following apparatus I have recently devised, and as it has not, as far as I know, been heretofore described, I think it is worth a short notice. It is a rule that applies to most chemical apparatus, and especially to gas generators, that the simplest is the best, and this requirement is certainly filled by the one here described.



It consists, as is seen from the accompanying figure, of a flask fitted with a cork with two perforations. Through one of these passes an ordinary outlet tube, and through the other a funnel tube with a Y attachment. On a rubber tube leading from the outlet tube is placed a pinchcock. The material is placed in the flask, the pinchcock opened, and acid added through the funnel tube. When it is desired to stop the operation it is only necessary to close the pinchcock, when the liquid will be forced up the funnel tube, and will flow out of the curved Y attachment into a vessel placed to receive it. From this it can be poured back into the flask when desired for use. Of course it is necessary for the funnel tube to reach to the bottom of the flask; and when this is the case it will carry out very nearly the last drop of acid, thus reducing to a minimum the waste of materials and the escape of gas into the room. If desired, a round-bottom flask supported by a stand may be used, as it will cause the last drops of acid to collect at the end of the funnel tube and be carried out.

Aside from its simplicity and the ease with which it is constructed, I have found this apparatus to work more satisfactorily than the more complicated forms. It will not become clogged with ferrous sulphate when used for generating hydrogen sulphide; nor after the pinchcock is closed can the generation of gas continue, from small lumps of the solid reagent dropping into the acid, as always happens to a greater or less extent in Kipp's and similar

forms of apparatus. Probably its chief advantage over most other forms is the ease with which the acid can be renewed.

J. R. DUGGAN.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, *March*, 1883.

Investigations upon the Relative Oxidability of Cast Iron, Steel, and Wrought Iron.

M. GRUNER gives the results of some long-continued experiments carried on by him upon the relative oxidability of cast iron, steel, and wrought iron, having in view the changes in rails, metallic constructions, and the hulls of vessels, by rusting and the action of sea water. It has been supposed by some engineers that this relative oxidability could be determined by submitting the different kinds of iron to the action of acidulated water. But it would be necessary to prove first that acidulated water produced the same effect as moist air or sea water, for the identity of action is not evident *a priori*.

In order to solve this question, M. Gruner made use of an apparatus consisting of a wooden framework, in which were suspended twenty-eight polished plates of steel and iron more or less hard or soft, pure or impure, each having a surface of a square decimeter. The plates were suspended by their corners 15 mm. apart, and by means of the framework could be simultaneously plunged into a bath containing acidulated water or sea water, or simply exposed to the action of moist air upon an open terrace. The plates were carefully cleaned and dried, and were weighed before and after each experiment.

The results obtained were as follows:

The experiments with moist air have not been continued long enough to decide whether the degree of carburation or the temper of the steels influenced or not the degree of corrosion by rust, and experiments upon this point are still in progress. Nevertheless the following points were determined: In twenty days the steels lost upon an average 3-4 grams per plate, the chrome steels were oxidised more, and the tungsten steels less, than the ordinary carbon steels. The cast irons were oxidised less than the steels and wrought irons, and among them the white specular iron (spiegel), containing 20 per cent. of manganese, less than the grey irons. The average loss in weight was about half that of the steels.

Sea water attacks iron, dissolving it like acidulated water, but under entirely different conditions. In a very short time chloride of iron is found in the bath. Unlike moist air, sea water attacks cast iron more strongly than steel, and white specular iron especially energetically. Thus in nine days, while the steels lost but 1-2 grams according to their nature, the white manganese iron lost 7 grams, the black iron, for the manufacture of Bessemer steel, 3.5 grams, and the phosphoric cast iron 5 grams. The tempered

steels were less attacked than the annealed, and the soft steels less than those containing manganese or chromium, and tungsten steel less than ordinary steel having the same percentage of carbon. Acidulated water, like sea water, dissolves grey iron more rapidly than steel, but not the white specular iron; the impure grey iron is the most strongly attacked. Thus in three days, in a bath of water containing .5 per cent. of sulphuric acid, renewed each day, the white specular iron lost 1.5 gram, pure charcoal iron .8 gram, and the steels from 1.1 gram to 4.1 gram.

The results of these experiments show that while, as regards chromium, manganese, and tungsten, the action of acidulated water is almost the same as that of sea water, in other respects it is entirely different, and is above all totally different from the action of moist air. Experiments with acidulated water can then show nothing as regards the relative resistance of different kinds of iron to the action of moist air or of sea water.—(*Comptes Rendus*, **96**, 195.) R. D. C.

On Oxidation in the Blood.

It is known that even arterial blood has scarcely more action than free oxygen on many substances which are readily oxidised when taken into the body. E. SALKOWSKI has devised a method of testing the oxidising power of blood under conditions which admit of very rapid and complete renewal of its oxygen. It consists in converting blood, to which various substances have been added, into fine spray by means of an atomiser, whereby a very large surface is exposed to the air and perfect oxygenation secured. The atomiser, holding about two and a half litres, is kept at a temperature of 40–42°, the spray being condensed in a large open cylinder and passed through the apparatus as often as desired. To make up for loss of water by evaporation, the blood is occasionally diluted with 0.6 per cent. sodium chloride solution. In the experiments described, the atomising of two or two and a half litres of blood required from one half to one hour, the process being repeated about sixteen times.

Hydrocinnamic acid (sodium salt) which is almost completely oxidised in the body to benzoic acid,[1] was recovered from the blood unchanged, no benzoic acid being detected. Benzene, which is oxidised in the body to phenol, pyrocatechin and hydroquinon,[2] though added frequently and carefully diffused, gave only traces of phenol. On the contrary, two and a half litres of blood, to which had been added two cc. of pure salicylic aldehyde, gave about .17 gram of salicylic acid, after being atomised for eight hours, although no special precaution was taken to prevent loss. A second experiment gave similar results. In two control experiments, in which

[1] Zeitschrift für physiologische Chemie, **7**, 168.
[2] Reichert and Du Bois Reymond's Archiv, 1867; Zeitschrift für physiologische Chemie, **4**, 336.

blood was replaced by water containing 0.6 per cent. sodium chloride and 0.2 per cent. sodium carbonate with 2 cc. of salicylic aldehyde, and in the second also gum arabic, to increase its viscosity, only traces of salicylic acid were obtained. The experiment was not made with blood serum. The author intends to apply the same method to blood containing other compounds of the aromatic and fatty series, especially to the carbohydrates, which, according to Nencki and Sieber,[1] are oxidised in alkaline solution by free oxygen.—(*Zeitschrift für physiologische Chemie*, **7**, 115.)

H. N. S.

On the liquefaction of oxygen and of nitrogen, and on the solidification of carbon bisulphide and of alcohol.

In a short note to M. Debray, MM. S. WROBLEWSKI and K. OLSZEWSKI give some account of their experiments upon the liquefaction of oxygen and nitrogen. The memorable experiments of Cailletet and Raoul Pictet upon the liquefaction of gases indicated the possibility of reducing oxygen to the liquid state in glass tubes, as may be done with carbon dioxide, provided a sufficiently low temperature could be obtained. About a year ago Cailletet recommended liquefied ethylene as a means of producing intense cold. This liquid, under the pressure of the atmosphere, boils at —105°, as measured by a thermometer containing bisulphide of carbon. Having compressed oxygen in a tube, and cooled it by means of liquefied ethylene to —105°, Cailletet observed, when some of the gas was suddenly allowed to escape, "a tumultuous ebullition which lasted for an appreciable time, and resembled the projection of a liquid into the cooled portion of the tube," but the liquid and gas could not be separated. Profiting by the experience of Cailletet, MM. Wroblewski and Olszewski made use of a new apparatus, by means of which a comparatively large amount of gas could be placed under a pressure of several hundred atmospheres, and proceeded to study the temperatures produced by the sudden escape of gases under pressure. Their investigation very soon led them to the discovery of a temperature at which carbon bisulphide and alcohol freeze, and at which oxygen is easily and completely liquefied. This temperature is obtained by allowing liquefied ethylene to boil in a vacuum. The temperature produced by this means is dependent upon the degree of the vacuum, the lowest temperature produced up to the present being —136°, as determined by the hydrogen thermometer. The critical temperature of oxygen is lower than the boiling point of liquefied ethylene under the atmospheric pressure, which is in fact not —105°, as has been stated up to the present, but between —102° and —103° as determined by the hydrogen thermometer. According to the experiments of MM. Wroblewski and Olszewski, oxygen commences to liquefy at a

[1] Journal für praktische Chemie [2] **26**, 140.

pressure of 26.5 atmospheres and temperature of —131.6°. Liquid oxygen is colorless and transparent like carbon dioxide. It is very mobile and forms a sharp meniscus. Carbon bisulphide freezes at about —116° and melts at —110°. Alcohol becomes viscous like oil at about —129°, and solidifies to a white mass at —130.5° A late dispatch from M. Wroblewski to M. Debray, dated April 16, says: "Nitrogen cooled, liquefied by sudden escape, meniscus visible, liquid colorless."—(*Comptes Rendus*, **96**, 1140.) R. D. C.

On the Foundations of Thermo-Chemistry.

The following paragraphs are taken from an article[1] by LOTHAR MEYER:

"It cannot have escaped the unprejudiced observer, that in spite of the large number of thermo-chemical observations, and in spite of the trustworthiness of a considerable proportion of the constants deduced from them, we can as yet scarcely speak of having a knowledge of chemical transformations based upon a thermo-chemical foundation. Although individual authors have attempted to develop this subject, the majority regard their investigations with doubt and uncertainty, if not with opposition; a fact which is surprising when we consider the high and undisputed respect which the mechanical theory of heat enjoys in our time. This may indeed arise partly from the fact that many an excellent chemist, in the effort to find methods for the preparation of new coloring or colorless compounds, does not spare the time necessary to assimilate the mass of results obtained in thermo-chemical investigations. It is also possible that many a one who has studied the subject has felt the necessity of caution, in consequence of the extreme care with which the master of thermo-chemical experimentation refrains from utilising for theoretical purposes the material which he has published by the volume .... However this may be, the principal reason why the thermo-chemical theory has thus far made so little headway is the fact that the majority of chemists justly feel that the subject is not yet sufficiently developed. ....

"As we cannot deny the validity of the principal laws of the mechanical theory of heat, the source of the contradiction must be sought for in an incorrect application of them. And here indeed, in my opinion, lies the whole cause of the present uncertain and uncomfortable condition of thermo-chemistry. We bother ourselves with old worn-out hypotheses and theoretical conceptions, which physics has long ago given up, and are then surprised that the world of reality does not conform to our preconceived notions which are based upon these dogmas.

"The first of these dogmas, but one which is as yet fraught with little danger, I see in the assumption that the atoms are particles *with attractive power acting through space*, while it is quite pos-

[1] Annalen der Chemie, **218**, 1.

sible, if not indeed highly probable, that everything which we call attraction is caused by certain motions of small particles, by impact or pressure. If this is also true of affinity, then the satisfying of affinity does not consist in a transformation of potential into kinetic energy, but union as well as separation of affinities are only transformations of one form of kinetic energy into another. This difference in conception is not a particularly great one, but it destroys the value of the conclusions that the separation of united affinities must necessarily be a production of *potential* energy, and that, on the contrary, a union of these affinities must be a transformation of potential into kinetic energy."

Molecular Weight of Haemoglobin.

Assuming that the compounds of haemoglobin (Hb) with oxygen (O_2), carbon monoxide (CO), and nitrous oxide (NO), contain 1 mol. haemoglobin to 1 mol. of gas, the molecular weight of haemoglobin can be determined if we know the exact volume of any of these gases with which a given weight of haemoglobin will combine. The attempts to determine the oxygen by dissociation of the compound HbO_2 *in vacuo* have not given concordant results, owing to the solubility of oxygen in water and the difficulty of obtaining perfect dissociation without partial decomposition of haemoglobin. By converting the compound HbO_2 into the more stable compound containing carbon monoxide and measuring the oxygen evolved, Hüfner[1] found, as the mean of ten determinations, that 1 gram haemoglobin (of the dog) combines with 1.202 cc. oxygen (0°, 1 meter pressure). MARSHALL, in Hüfner's laboratory, has recently determined the volume of carbon monoxide in the haemoglobin compound by shaking a solution containing a known weight of the compound with nitrous oxide, whereby the carbon monoxide is expelled and the compound with nitrous oxide formed. The residual gas was collected and the evolved carbon monoxide determined after removal of excess of nitrous oxide by oxygen and water. The apparatus and method employed were essentially those of Hüfner.[2] The advantage of Marshall's method consists in the comparatively great stability of the compounds of haemoglobin with carbon monoxide and with nitrous oxide, and in the slight solubility of carbon monoxide in water. Marshall finds, as the mean of ten experiments, that 1 gram of dog's haemogoblin combines with 1.205 cc. carbon monoxide (0°, 1 meter pressure), giving as the molecular weight of HbCO 14157, whence he deduces the formula:

$$C_{637}\ H_{1025}\ N_{164}\ Fe\ S_3\ O_{190}\ !$$

—(*Zeitschrift für physiologische Chemie*, **7**, 81). H. N. S.

[1] Journal für praktische Chemie [2] **22**, 385. [2] *Ibid.* 383.

ERRATUM.—Page 41, last line, read *nitrite* for *nitrate*.